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A PROCESS FOR THE EFFICIENT CONVERSION OF WASTE PINE TO ETHANOL

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PREFACE

This document constitutes the final report for work carried out as a joint venture between Bio-hol Developments (Downsview, Ontario, Canada), the Tennessee Valley Authority (Muscle Shoals, Alabama, USA), the Swedish Ethanol Development Foundation (Ornskolsvik, Sweden), and the Department of Energy, Mines and Resources (Ottawa, Ontario, Canada) entitled "A Process for the Efficient Conversion of Waste Pine to Ethanol". The project was carried out over a period of two years.

The purpose of the work was to establish operating conditions and identify the process equipment necessary for the conversion of pine into ethanol. The project has significance in the utilization of renewable resources and waste lignocellulosic materials for the production of fuel ethanol, and will be of importance to those involved in the fields of energy production, environmental waste reduction, and also to the pulp and paper industry.

ABSTRACT

The primary objective of the project was the development and optimization of a process for the conversion of waste pine into ethanol. A two-stage weak acid hydrolysis system formed the basis of a comprehensive process design (CASH Process). The project was carried out as an international effort between Canadian (Bio-hol), American (TVA) and Swedish (SEDF) groups.

With TVA's Sunds defibrator/digester, conversion of the hemicellulose portion of the pine chips to its component sugars exceeded 90% of the theoretical. The washed residue of this prehydrolysis was sent to Bio-hol where extensive second stage hydrolysis tests were conducted using a pilot-scale plug flow reactor. The effect of the reaction conditions on both glucose yield and fermentability was studied in great detail. Cellulose-to-glucose conversions in the 40-50% range were achieved. The resulting hydrolysates were fermented at concentrations up to 12%, although usually in the 6-8% range. A process organism was selected based on its resistance to and its ability to acclimatize itself to both hemicellulose and cellulose hydrolysates. This specially acclimatized strain of *S. cerevisiae* was named the CASH1 strain.

Fermentation trials were carried out on 50/50 mixtures of cellulose and hemicellulose hydrolysates both on a lab scale (1L) and a pilot-plant scale (100L). Ethanol yields and sugar utilization rates for the mixed hydrolysate fermentations were comparable to those for corresponding control fermentations. The ethanol yield was typically 92% of the theoretical. The inhibitory effects of the wood hydrolysates were primarily evident during cell growth. The pilot-scale fermentations confirmed the kinetic parameters that were measured on the lab scale.

The mass balance using base case process parameters, for a CASH process plant fed with 100,000 tonne/year (dry basis) pine sawdust, produced an ethanol yield of 22,400 m^3/year. A stand-alone CASH facility could produce ethanol for $0.93/L while a coupled facility could produce ethanol for $0.65/L. If the optimal process conditions were achieved, the plant ethanol yield would be 27,479 m^3/year and the unit price of ethanol (with a zero feedstock cost) would be $0.40/L.

The project was significant because it was perhaps the first complete effort which studied each process area of a lignocellulosic-to-ethanol plant. In particular, the relationship between reaction conditions, glucose yield and hydrolysate fermentability was examined carefully. All major process assumptions (especially those relating to fermentability) were confirmed with pilot plant and lab trials.

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EXECUTIVE SUMMARY

This project was initiated to examine the production of alternative fuels (ethanol) from renewable resources (pine). The technology to be examined involved the conversion of the components of pine to sugars, followed by fermentation of the resulting sugars to ethanol.

The major objective of the project was to establish optimal operating conditions and identify the process equipment necessary for the conversion of pine into ethanol. The successful completion of the project is a key step in providing a Canadian commercial technology which is marketable worldwide.

The project was performed as a combined effort between Canadian (Bio-hol), American (Tennessee Valley Authority), and Swedish (Swedish Ethanol Development Foundation) groups. Bio-hol was involved in the process design and conducted pilot-scale examinations of cellulose hydrolysis, separation, and fermentation. TVA optimized the hemicellulose hydrolysis process and provided engineering expertise. The SEDF provided the engineering drawings and the mass balance/economic model.

The optimum operating conditions for the SO_2-catalyzed hemicellulose hydrolysis of pine chips were established using TVA's Sunds Defibrator. Yields of hemicellulose sugars exceeding 90% of the theoretical were obtained.

Optimization of the plug flow reactor conditions for the hydrolysis of the cellulose portion of the wood comprised a significant portion of the work. Cellulose-to-glucose conversions of over 50% were achieved, and, according to the kinetics of dilute-acid hydrolysis, a cellulose-to-glucose conversion of 50% is very close to the maximum attainable. This maximal yield exists because glucose is the intermediate product in a series of consecutive reactions (i.e., cellulose --> glucose --> degradation products). The fermentability of the resultant hydrolysate was of overriding importance in selecting the best operating conditions. Conditions of high temperature, short residence time, and low acid concentration were chosen to be optimal for cellulose to glucose conversion. These reaction conditions produced fermentable hydrolysates with cellulose-to-glucose conversions of 40 to 50%.

The separation of the soluble stream (sugar solution) from the lignin/cellulose residue of the process was complicated by the fineness of the residual solids. A scroll-type decanter/centrifuge performed the task well, provided that the feed flow, solids content, and temperature were set at their determined optimal levels.

Pilot-scale dryer tests showed that the hydrolysis residue was relatively simple to process. The product was dried to over 95% dry solids and left no deposits in the dryer unit. This dried residue is a high fuel-value co-product of the process.

Wood hydrolysates (i.e., sugar solutions produced from the carbohydrate polymers of wood) tend to be toxic or inhibitory to the fermentation process carried out by most ethanol-producing microorganisms. Ten strains of the yeast *Saccharomyces cerevisiae*, along with the bacterium *Zymomonas mobilis* and the yeast *Pichia stipitis*, were evaluated as possible process microorganisms. Based on its resistance to wood-derived inhibitors and its ability to grow on both hemicellulose and cellulose hydrolysates, a strain of *Saccharomyces cerevisiae* was selected. This strain was acclimatized to cellulose hydrolysate and became known as the CASH1 strain.

Small-scale (1L) batch fermentations were carried out using 50/50 mixtures of hemicellulose and cellulose hydrolysates. Synthetic mixtures of pure sugars, which corresponded to the levels occurring in the hydrolysate mixture, were used for control fermentations. Although the hydrolysate mixtures had slightly lower rates of sugar utilization and ethanol production than the controls, it appeared that the inhibitory effects of the wood hydrolysates were manifested primarily during cell growth. Ethanol yields were typically 92% of the theoretical. Pilot-scale (100L) fermentations of the 50/50 mix of hemicellulose and cellulose hydrolysates showed sugar utilization rates, ethanol production rates, and cell growth rates which corresponded to those in the lab fermentations. Each of the pilot runs were complete within approximately 30 hours. These pilot runs were carried out with initial sugar concentrations of approximately 50 g/L. However, given that lab-scale fermentations were performed successfully with sugar concentrations in the 70-80 g/L range and the data from the pilot-scale fermentations closely agreed with corresponding lab fermentations, it is believed that these higher sugar concentrations could also be fermented at the larger scale.

A complete process (CASH) for the production of ethanol from waste wood (or other lignocellulosic feedstock) was designed as a joint effort between the Canadian, American, and Swedish groups. A mass balance and economic analysis was carried out using a computer program developed by the SEDF. A "stand-alone" CASH process plant was found to produce ethanol at a cost of $0.93 per litre. Such a facility would not be feasible based on economic considerations alone (although it should be emphasized that the positive environmental impacts (and associated savings) must also be taken into account). However, if the CASH process plant is integrated or "coupled" with an existing facility, the ethanol cost is $0.65/L. If the scale of the plant is doubled, the cost of the ethanol produced drops to $0.48/L. Sensitivity analyses on the "coupled" facility show that the annual production cost is very dependent on feedstock cost. If the feedstock cost is reduced to zero, the ethanol cost would be $0.47/L. If the best achievable process parameters are attained in the production facility, and with a zero feedstock cost, the cost of the ethanol produced falls to $0.40/L.

Some of the findings of the project (especially regarding process conditions, yields and fermentabilities) may be somewhat feedstock specific, so it was recommended that the process alterations necessary to accommodate other feedstocks (such as waste paper, waste fibre streams from pulp mills, and various hardwoods and agricultural residues) be studied in the future. The fermentation of pentose sugars could significantly improve process ethanol yield so it was recommended that research in this area should continue. The CASH process could readily accommodate a different organism should a pentose-fermenting strain which is tolerant to wood hydrolysates be developed.

The project combined process design with a detailed examination of process variables on a pilot-plant scale. Virtually all of the assumptions made during the process design were confirmed with pilot or lab tests. This unique and complete approach provided extensive knowledge relative to the process conditions and yields that were reasonably achievable in a facility of this kind. From an environmental perspective, the project was important because its basis was the utilization of waste materials and renewable resources for the production of an alternative fuel. The positive environmental impacts of ethanol as a fuel are well-documented and represent a further benefit of the project.

RÉSUMÉ

Ce projet a été entrepris en vue d'examiner la production de carburants de remplacement (éthanol) à partir de ressources renouvelables (bois de pin). La technologie qui sera examinée comporte la conversion des constituants du bois de pin en sucres, puis la fermentation en éthanol des sucres ainsi obtenus.

L'objectif principal du projet était de déterminer les conditions optimales de production et le matériel nécessaire à la conversion du bois de pin en éthanol. La réalisation avec succès de ce projet constitue une étape clé de la mise au point d'une technologie canadienne commercialisable à l'échelle mondiale.

Le projet a été réalisé grâce aux efforts concertés de groupes canadien (Bio-hol), américain (Tennessee Valley Authority) et suédois (Fondation suédoise pour le développement de l'éthanol). La Bio-hol a participé à la conception du procédé et a effectué des études à l'échelle pilote de l'hydrolyse, de la séparation et de la fermentation de la cellulose. La Tennessee Valley Authority (TVA) a optimisé le procédé d'hydrolyse de l'hémicellulose et a fourni son expertise technique. La Fondation suédoise pour le développement de l'éthanol (FSDÉ) a fourni les dessins ainsi que le modèle de bilan massique/économie.

À l'aide du défibreur Sunds de la TVA, nous avons établi les conditions optimales pour l'hydrolyse catalysée par le SO_2 de l'hémicellulose de copeaux de bois de pin. Les rendements en sucres hydrolysables en hémicellulose étaient supérieurs à 90 %.

L'optimisation des conditions d'écoulement à bouchons dans le réacteur pour l'hydrolyse de la partie cellulosique du bois a constitué une part importante des travaux. Nous avons obtenu des taux supérieurs à 50 % pour la conversion de la cellulose en glucose; selon la cinétique de l'hydrolyse en acide dilué, un taux de conversion cellulose-glucose de 50 % est très proche du taux maximum possible. Ce taux maximum de conversion est imposé par le fait que le glucose constitue un produit intermédiaire dans une série de réactions consécutives (c.-à-d. cellulose glucose produits de dégradation). La fermentescibilité de l'hydrolysat obtenu était le facteur le plus important dans le choix des conditions optimales. Nous avons choisi une température élevée, un court temps de séjour et une faible concentration d'acide pour obtenir un taux optimal de conversion cellulose-glucose. Ces conditions de réaction permettent d'obtenir des hydrolysats fermentescibles avec des taux de conversion de 40 à 50 %.

La finesse des résidus solides rendait plus difficile la séparation des substances solubles (solution de sucres) du résidu constitué de lignine et de cellulose. On pouvait efficacement effectuer cette séparation avec un décanteuse continue à axe

horizontal, à la condition de régler le débit d'alimentation, la teneur en solides et la température à la valeur optimale déterminée.

Des essais de séchage à l'échelle pilote ont révélé que le traitement du résidu d'hydrolyse était relativement simple. On a séché le produit jusqu'à une teneur en solides secs de plus de 95 %, et il n'y avait aucun résidu de séchage. Le résidu séché est un sous-produit à pouvoir calorifique élevé.

Les hydrolysats de bois (c.-à-d. les solutions de sucres obtenues à partir des chaînes de glucides qui constituent le bois) ont tendance à inhiber la plupart des micro-organismes qui produisent de l'éthanol, ou à être toxiques pour ceux-ci. Nous avons évalué dix souches de la levure Saccharomyces cerevisiae, ainsi que la bactérie Zymomonas mobilis et la levure Pichia stipitis pour déterminer dans quelle mesure elles pouvaient être utilisées à cette fin. Nous avons choisi une souche de Saccharomyces cerevisiae, car celle-ci résistait aux inhibiteurs tirés du bois et pouvait être cultivée sur des hydrolysats d'hémicellulose et de cellulose. Cette souche, qui s'est acclimatée à l'hydrolysat de cellulose, a été désignée par le terme souche CASH1.

Nous avons effectué des fermentations en petits lots (1 L) en utilisant des mélanges 50/50 d'hydrolysats d'hémicellulose et de cellulose. Nous avons utilisé, comme milieux de fermentation témoins, des mélanges synthétiques de sucres purs dont les concentrations correspondaient aux concentrations dans le mélange d'hydrolysats. Même si les mélanges d'hydrolysats présentaient des vitesses d'utilisation de sucres et de production d'éthanol légèrement plus faibles que les témoins, les effets inhibiteurs des hydrolysats de bois se manifestaient principalement, semble-t-il, pendant la période de croissance cellulaire. Les rendements en éthanol étaient typiquement de 92 %. Les taux d'utilisation de sucres, de production d'éthanol et de croissance cellulaire au cours de fermentations à l'échelle pilote (100 L) du mélange 50/50 d'hydrolysats d'hémicellulose et de cellulose correspondaient à ceux mesurés au cours de fermentations réalisées en laboratoire. Chaque série de fermentations à l'échelle pilote nécessitait environ 30 heures. Au cours de ces séries de fermentations, la concentration initiale de sucres était d'environ 50 g/L. Toutefois, comme les fermentations en laboratoire donnaient de bons résultats avec des concentrations de sucres de 70 - 80 g/L et que les données obtenues au cours des fermentations à l'échelle pilote concordaient étroitement avec celles obtenues au cours des fermentations en laboratoire, il serait aussi possible, estime-t-on, de procéder à la fermentation à une plus grande échelle de ces solutions plus concentrées.

Grâce aux efforts concertés des groupes du Canada, des États-Unis et de Suède, nous avons mis au point un procédé complet (CASH)

permettant de produire de l'éthanol à partir de déchets de bois. Nous avons déterminé le bilan massique et procédé à une analyse économique à l'aide d'un programme informatique élaboré par la FSDÉ. On a constaté qu'une usine fonctionnant seule et utilisant le procédé CASH produisait de l'éthanol au coût de 0,93 $ le litre. Une telle installation ne serait pas rentable si l'on tient compte uniquement des aspects économiques [mais, soulignons-le, il faut aussi tenir compte des avantages pour l'environnement (ainsi que des économies qui en découlent)]. Toutefois, si on intègre ou si on "apparie" l'usine exploitant le procédé CASH avec une installation existante, on diminue le coût de production d'éthanol à 0,65 $ le litre, et ce coût tombe à 0,48 $ le litre si on double l'échelle de l'usine. Si on réduit à zéro le coût de la charge d'alimentation, le coût de production d'éthanol tombe à 0,47 $ le litre. Une installation alimentée avec une charge de départ de coût nul et dont les paramètres du procédé seraient les meilleurs possibles produirait de l'éthanol au coût de 0,40 $ le litre.

Certaines des constatations faites au cours du projet (plus particulièrement celles relatives aux conditions, aux rendements et aux fermentescibilités) peuvent dépendre quelque peu de la charge d'alimentation; c'est pourquoi il a été recommandé d'étudier ultérieurement les modifications qu'il faudrait apporter au procédé pour qu'il puisse accepter d'autres charges d'alimentation (comme déchets de papier, déchets de fibres des usines de fabrication de pâte, divers bois de feuillus et résidus agricoles). Comme la fermentation de pentoses pourrait améliorer considérablement le rendement en éthanol, il a été recommandé de poursuivre les recherches dans ce domaine. Le procédé CASH pourrait facilement utiliser un organisme différent, si une souche permettant de fermenter les pentoses et tolérant les hydrolysats de bois était mise au point.

Au cours du projet, on a étudié la conception du procédé tout en examinant de façon détaillée les variables à l'échelle pilote. Pratiquement toutes les hypothèses formulées au cours de la conception du procédé ont été confirmées lors d'essais réalisés à l'échelle pilote ou en laboratoire. Cette approche unique et complète a fourni de nombreuses informations sur les conditions du procédé et sur les rendements qu'il permet raisonnablement d'obtenir dans une installation de ce type. Le projet était important du point de vue environnemental, car il comporte la production d'un carburant de remplacement à partir de déchets et de ressources renouvelables. Les impacts positifs pour l'environnement de l'utilisation de l'éthanol comme carburant sont bien documentés et constituent un autre avantage de ce projet.

1. INTRODUCTION

1.1 CASH Process

The CASH process (Canada, America, Sweden, Hydrolysis), described in this report, is the result of combined development work on a two-stage weak acid hydrolysis process for the production of fuel or industrial grade ethanol utilizing lignocellulosic materials as the feedstock. Almost all of the hemicellulose and more than 50% of the cellulose contained within the feedstock are converted to sugars which may be fermented to produce ethanol. A mixture of lignin and unhydrolyzed cellulose is a co-product which has a higher energy content (per unit weight) than the starting material. At present, the CASH process only includes hexose fermentation. The pentoses released from the hydrolysis of the hemicellulose end up either in the lignin fuel or in the effluent water. The organic component of the sewage system from a plant based on the CASH process can be converted to methane gas by anaerobic fermentation. The methane can be used as a fuel to generate process steam.

The overall objective of this project was the development of a continuous process for the economical production of fuel grade ethanol from waste pine chips or sawdust. The hexose sugars of pine hemicellulose and cellulose hydrolysates were to be fermented using *Saccharomyces cerevisiae*. The most apparent barrier to this objective was the toxicity of these acid hydrolysates to yeasts. The selection of tolerant yeast strains, acclimatization of the strains to increase their tolerance, and treatment of the hydrolysates to diminish toxic effects were among the strategies used to aid in overcoming this barrier.

It is well known from the literature that the conditions used for the dilute acid hydrolysis of hemicellulose result in minimal yields of available hexose sugars (virtually all of the potential glucose is left as unreacted cellulose), while the harsh conditions required for the hydrolysis of cellulose result in the degradation of the hemicellulose-derived sugars. To overcome this, the CASH process utilizes a two-stage dilute acid process, which features the hydrolysis of both the hemicellulose and cellulose components separately. The first stage is a "mild" reaction aimed at the solubilization of the amorphous hemicellulose portion into its component sugars. After removal of the sugars generated in this first-stage reaction, more "severe" reaction conditions are used to convert the cellulose to glucose.

Conditions for the hydrolysis of hemicellulose using mild acid had been previously established by the Tennessee Valley Authority (TVA, Muscle Shoals, Alabama) (Westmoreland *et al.*, 1988). However, it was necessary to determine the optimum conditions for cellulose hydrolysis using a continuous plug flow reactor. This work was carried out at Bio-hol Developments (Ontario, Canada), and included an examination of the effect of temperature, acid concentration, and reaction time on the yield of glucose from cellulose. It was also imperative that the product be fermentable. Thus, the conditions which resulted in the best cellulose-to-glucose conversions, while producing a fermentable substrate, were considered optimal. Also carried out by Bio-hol were lab and pilot-scale fermentation studies and tests involving liquid/solid separation. The development of process flow diagrams and a mass balance/economic model of the process were carried out by the Swedish Ethanol Development Foundation (SEDF), in consultation with TVA and Bio-hol.

1.2 Potential for Ethanol

Ethanol is a very versatile chemical that can be used in a wide range of applications. It is used as a technical product, an intermediate raw material for the chemical industry, and as a motor fuel. Ethanol is used as a solvent/diluent in lacquers and paints. More applications for ethanol may develop, at the expense of other solvents, as a result of its positive environmental qualities. Ethanol is also used as an extraction and leaching agent in the synthesis of pharmaceuticals. Familiar applications within the automotive industry, particularly in cold climates, include windshield washer fluid and carburetor antifreeze.

Up until the Second World War and the commercial breakthrough by petrochemical-based feedstocks, ethanol served as one of the most important raw materials for the chemical industry. Even ethylene was produced primarily from ethanol during this pre-war period. The production of important final products such as acetaldehyde, ethyl acetate, acetic acid, glycols, and even synthetic rubber were formerly ethanol-based. Some of these compounds could be competitively produced from ethanol. In the long term, ethanol may see a renaissance as an important feedstock for the chemical industry.

The main focus for expansion of the ethanol industry during recent years has been ethanol's potential as a motor fuel. Ethanol can be used in gasoline as an octane booster,

as a fuel extender, or it can be used as a neat fuel. Ethanol can also replace diesel, either neat or in mixtures with diesel fuel.

The production of ethanol from renewable resources has the significant benefit of providing a plentiful domestic supply of an environmentally clean motor fuel that can replace imported fossil fuels. The world resources of fossil (non-renewable) reserves are limited. The transportation sector is almost fully dependent on fossil fuels, and is expected to use an increasingly larger portion of the world's energy in the future. Thus, there is an emphasis on alternative fuels including ethanol.

1.3 Raw Materials for Ethanol Production

Aside from petroleum-based ethylene, almost any carbohydrate-containing material can be used as a source of fermentable monomeric sugars from which ethanol can be produced. The traditional renewable raw materials for ethanol production have been sugar and starch crops, such as corn and various grains. These types of raw materials still represent the predominant feedstocks for ethanol production from renewable materials. At the same time, the production of ethanol from these feedstocks has been highly debated and criticized for different reasons. The production of fuel ethanol from these relatively expensive feedstocks, which has taken place mainly in Brazil and the United States, has been spurred by various government subsidies and incentives. Nevertheless, the development of a market for ethanol as an automotive fuel might be justified for environmental and other reasons which are difficult to evaluate from strictly an economic perspective.

Over the last several decades, much work has been devoted to developing commercial processes for the manufacture of ethanol from lignocellulosic raw materials. These potential feedstocks are comprised of carbohydrate polymers known as hemicellulose and cellulose, as well as lignin and minimal levels of other compounds. Undervalued trees, forestry residues, sawdust, and industrial and household cellulosic wastes can be included in this array of largely under-utilized feedstocks. At present, the majority of these materials are not used at all.

1.4 Environmental Aspects

Ethanol produced via the CASH process has significant positive impacts on the environment. The feedstocks are either residues or wastes with little or no value, and very few alternative uses. A CASH ethanol plant can be designed with very little negative impact on the environment.

The carbon dioxide created by the burning of fossil fuel adds to the greenhouse effect and threatens to change the climatological patterns of the earth. Conversely, the production of ethanol from renewable raw materials results in no net production of carbon dioxide. The carbon dioxide released during fermentation and combustion of ethanol is consumed during the growth of the trees which feed the process. Thus, ethanol utilization does not contribute to the net accumulation of carbon dioxide in the atmosphere and the associated global climate change. The use of ethanol as a fuel has other benefits with regard to lowering emissions such as photochemical smog, aerosol particles, carbon monoxide, hydrocarbons, sulphur oxides, nitrogen oxides, etc.

1.5 Energetics

The production and use of ethanol has been criticized from an energy balance point of view. Some sources say that the production of ethanol requires more energy than is contained in the final product. No transformation is possible between different forms of energy without losses of energy. Such losses are, however, acceptable, if the resultant form of energy has more potential applications and the process allows for the transformation of unused waste materials into beneficial value-added products.

The CASH process to produce ethanol from lignocellulosic raw materials is flexible with regard to possible feedstocks. The cheapest raw materials are surplus materials from logging, saw mills, industrial and household waste fibre, etc.

In the CASH process, an energy-rich co-product is produced along with the ethanol consisting of lignin and approximately 20-30% cellulose. This solid fuel product can be sold as a substitute for coal and heating oil. The wastewater treatment in the CASH process consists of an anaerobic fermentation system which produces methane gas from

organic compounds in the plant's wastewater stream. The methane gas can be used to produce some of the steam necessary for the hydrolysis, distillation and drying steps of the CASH process.

Fermentation of the pentoses produced through the hydrolysis of lignocellulosic material could further increase the yield of ethanol from lignocellulosic feedstocks. Depending on the starting materials, the utilization of the pentoses could increase the ethanol production by 10-50 %. Research work to solve the pentose fermentation problem continues in various institutions around the world. A commercial solution is expected in the near future.

The CASH ethanol process may already be commercially viable. The economics are dependent on the feedstock costs, the cost of energy used, plant size, co-product income and by-product credits. The process is based on proven commercial unit operations. The process design is flexible enough to accommodate future technology, once it is ready to merge with the CASH process.

1.6 Production Routes: Historical Aspects

A study of the history of wood-to-ethanol processing was carried out at the outset of the development of the CASH process. This was done to learn from previous experiences, to utilize past successes, and to accelerate the effort to develop a modern, economical process for the production of ethanol from wood-derived sugars.

The idea of producing ethanol from wood can be traced back to 1819, when Braconnot (1819) discovered that cellulose could be converted to fermentable sugar by treatment with concentrated mineral acid. Based on this discovery, Simonsen (1898) conducted research on wood hydrolysis. Early commercial experience in the production of ethanol from lignocellulosic materials was based on acid hydrolysis. With few exceptions, such facilities were built because of special circumstances.

1.6.1 First Commercial Experience

The first commercial production of ethanol from wood sugars took place in the United States during World War I. Ewen and Tomlinson built plants in Georgetown, South Carolina, and Fullerton, Louisiana (Saeman, 1982). These factories used pine sawdust as the raw wood material. The catalyst used in this dilute acid hydrolysis process was sulphuric acid. The process consisted of a one-stage digestion, with subsequent sugar removal in an extraction battery. At approximately 90 litres of ethanol per metric ton of wood feedstock, the yield in these factories was very low. However, because the cost of the sawdust was very low and there were no environmental controls required, the factories were profitable during the war.

1.6.2 Scholler Process

The original Scholler process plant was built at Tornesch, Germany, with the first wood hydrolysis reactor installed in 1931. The main difference between the Scholler process and the first industrial process mentioned above, was that batches of dilute sulphuric acid were percolated through a column of wood shavings and sawdust, as opposed to batch digestion and subsequent extraction in another vessel (Locke *et al.*, 1945).

The feedstock was charged into the Scholler percolator and then compressed with steam. This charging procedure was generally repeated three times to insure maximum utilization of the percolator volume. The wood charge was then heated. After approximately one hour of heating, dilute sulphuric acid was charged to the percolator, the entire mass was heated, and the sugar-containing liquid stream was then removed from the bottom of the reactor. This procedure was repeated 12 to 20 times, depending on the nature of the wood charge. Total percolation time could exceed 24 hours. After the sugar solution was produced, it was held at 100°C for a period of about 12 hours to post-hydrolyze the carbohydrate oligomers to monomeric sugars. The Scholler percolators were constructed from lead-lined carbon steel shells with an internal layer of acid-resistant brick.

Fermentation of wood sugars was carried out in a series of three fermenters (cascade fermentation). The sugar content of the medium was approximately 6 per cent,

with two-thirds of the sugar originating from the wood process, and the remainder coming from beet sugar. The residence time required for fermentation was four to six hours. The ethanol yield per ton of wood fed to the Scholler percolator was approximately 210 litres, as compared to 90 litres per metric ton in the original American process. At the end of World War II, there were Scholler plants in Tornesch, Holzminden, and Dessau, Germany. There was also one plant in Korea, one in Ems, Switzerland, and one under construction near Florence, Italy.

Except for the Swiss factory, which operated until 1956, these ethanol-from-wood facilities were shut down at the end of World War II. These factories were not economical because of the lack of abundant cheap wood supplies and the development of a new process for synthesizing ethanol from ethylene.

In 1935, the Scholler process was introduced in the USSR. Currently, there are reported to be more than 40 wood hydrolysis plants operating in the USSR which had their origin from the Scholler process. In addition to ethanol, these plants produce fodder yeast, furfuraldehyde, and xylitol.

1.6.3 COALBRA Process

Russian technology was exported to a Brazilian company in 1985. The name of the Brazilian company was COALBRA, an acronym for the Portuguese words for coke and alcohol company. The products were to be ethanol, furfural, animal feed and lignin coke. An entire factory was fabricated in the USSR and shipped to Brazil. As a result of Soviet improvements, the equipment and process were somewhat different from that used originally at Tornesch, Germany. The hydrolysis reactors were constructed from titanium instead of carbon steel, lead, and acid brick. The wood feed was in chip form, instead of sawdust and shavings, thus reducing the time required to fully load the reactor. Instead of many successive batches (12 to 20) of acid, one batch of acid was used to impregnate the charge and another was used for percolation. As a result, the overall processing time was reduced to approximately 6 hours.

The COALBRA facility began operation in 1985 and only operated as an ethanol producing factory for about one year. It operated for approximately one more year as a

furfural producing factory. Reportedly, ethanol production was not very satisfactory, but the production of furfural was profitable. Also during this time, the need for ethanol from wood declined, primarily as a result of better than anticipated efficiency with other means of ethanol production (e.g., sugar cane). Nevertheless, there was enough promise from this first facility that work is still being done in Brazil to produce ethanol and other chemicals from wood. Another facility using a continuous hydrolyzer is being planned.

1.6.4 Bergius-Haaglund Process

Willstatter and Zechmeister published the discovery that, at ordinary temperatures, 40 per cent hydrochloric acid readily solubilizes cellulose (Shreve, 1956). Bergius and Haaglund developed a factory in 1933 at Mannheim-Rheinau, Germany, using hydrochloric acid to process wood to sugar for the subsequent production of yeast. By the end of the Second World War, this factory was using sulphite pulp, corn cobs, and oat hulls, as well as wood, to produce crystalline glucose, fodder yeast, bakers yeast, and furfural. Sugar yields from cellulose in the Bergius-Haaglund process were superior to those in the Scholler process. However, the equipment was much more expensive. Some of the materials of construction used for the equipment in these plants were Haveg, ceramics, rubber-lined steel, and acid-resistant bricks. Evaporator tubes were either gold or platinum-coated copper. Corrosion considerations were much more significant than in the Scholler process (Locke *et al.*, 1945). Since these plants were shut down, there have been no other attempts to commercialize a process using 40 per cent hydrochloric acid. However, dilute hydrochloric acid has been successfully used for commercial starch hydrolysis.

1.6.5 Cederquist Process

Dr. Karl N. Cederquist, working for Stora Kopparberg, headed a research team at Falun, Sweden that started work on wood hydrolysis in the 1930s. This work continued through World War II. There were two basic new ideas tested by Dr. Cederquist. One was performance of the hydrolysis in two stages, so that the hemicellulose and cellulose were hydrolyzed separately. There was a liquid-solid separation step between the two stages, so hemicellulose sugars were extracted prior to cellulose hydrolysis. This preserved

the sugars made from the hemicellulose (primarily pentoses if deciduous trees were used for feedstock) and prevented the formation of the fermentation inhibitor furfural during cellulose (second stage) hydrolysis. The other hypothesis tested by Cederquist was the use of shorter residence times and higher temperatures for these hydrolysis steps. The shorter residence times offered lower capital costs and some possibility for yield improvement. The work was done using sawdust at a throughput of approximately 50 tons per day. The reactors were rotating globe digesters that were heated by live steam injection (Cederquist, 1954).

1.6.6 Madison Process

The Forest Products Laboratory of the United States Department of Agriculture in Madison, Wisconsin, began work to develop a process for producing ethanol from wood during World War II. They used the Scholler process as a starting point. Improvements were made in the way that acid was added and removed. The cycle time was about 20 per cent of that for the original Scholler process. The Madison process was reportedly adopted by the USSR and is essentially the process utilized by COALBRA. Work was begun to build a commercial facility based on the Madison process in 1944. This facility was constructed at Springfield, Oregon, US, and was completed in 1947 (Gilbert, 1952). Much of the demand for ethanol in the US during World War II was as a starting material for synthetic rubber. When the war ended and there was ample natural rubber available, the demand for ethanol decreased.

1.6.7 Sulphite Liquor Process

The sulphite pulping process for paper manufacture is second to the sulphate (Kraft) process on the basis of quantity of pulp produced. In this process, the hemicellulose and lignin are dissolved to produce the cellulose pulp. About one-half of the wood is dissolved in this process. The spent liquor containing the hemicellulose sugars can be processed to produce ethanol.

The first large-scale fermentation of sulphite liquor sugars was done in 1909 at Skutskar, Sweden. This practice was then extended to many other sulphite pulp mills to

reduce pollution and provide more income. Ordinary bakers yeast, *Saccharomyces cerevisiae* Hansen, is suitable for this fermentation. Initially, this yeast ferments glucose and mannose and, after adaptation, the yeast also ferments galactose. There has been no commercial fermentation of pentoses, so conifers, which yield predominantly hexoses when hemicellulose is dissolved, are the preferred feedstock for sulphite liquor to ethanol fermentation. The yield of ethanol varies tremendously, depending on the type of wood feedstock and the processing conditions used (the basic sulphite process does not change, but cooking time and temperature are varied). The ethanol yield generally varies from 25 to 70 litres per metric ton of wood feedstock (Rydholm, 1965).

1.7 Theory of Acid Hydrolysis of Cellulose

Much like the historical perspective discussed previously, reviewing the theory of acid hydrolysis of cellulose was a useful exercise for several reasons. First, the nature of the reaction and the limitations that exist were seen. Second, insight was obtained into the trends expected in our own experimental data. This provided a head start in determining the optimum reaction conditions. Third, feedback was provided as to whether the yields achieved were reasonable.

The pseudo first-order reactions which take place are represented by the following sequence:

$$\text{CELLULOSE} \xrightarrow{k_1} \text{GLUCOSE} \xrightarrow{k_2} \text{BREAKDOWN PRODUCTS}$$

The kinetics of series reactions are such as to limit the possible yield of the intermediate product (i.e., glucose). Thus, there exists a maximum attainable yield of glucose. The size of this maximum is controlled by the relative rates of the two reactions shown above. The rates are determined by the pseudo first-order rate constants k_1 and k_2. These are, in turn, related to the reaction temperature and the acid concentration in the slurry. Reaction time is an external factor which controls the extent of reaction which takes place once the rate constants have been set.

In general, for a series reaction such as this, the expression for the yield of the intermediate product is:

$$C_B/C_{A0} = (k_1/(k_2-k_1))*(\exp(-k_1t)-\exp(-k_2t))$$

where a = cellulose
b = glucose

The maximum achievable yield of the intermediate and the time at which it occurs are given by:

$$C_B/C_{A0MAX} = (k_1/k_2)^{(k1/(k2-k1))}$$
$$t_{OPT} = \ln(k_2/k_1)/(k_2-k_1)$$

For a given temperature and acid concentration, the rate constants are set and thus, the maximum glucose yield is set. The magnitude of this maximum can only be changed by altering k_1 and k_2, but the actual yield achieved varies significantly with reaction time. That is, time does not control the size of the maximum yield but only whether this "pre-set" maximum will be achieved. Note that for the dilute acid hydrolysis of cellulose, because the first reaction has a higher activation energy than the second reaction, high reaction temperatures (and necessarily corresponding short reaction times) favour the first reaction over the second (Grethlein and Converse, 1982).

A conceptualized product distribution versus time for the acid hydrolysis of cellulose (at specific conditions of temperature and acid concentration) is shown in Figure 1. This figure is only representative (i.e., peaks shown are not actual) and is included for discussion purposes. Note that the peak glucose concentration may be fairly broad and may encompass quite a range of extents of cellulose conversion. Thus, the characteristics of two hydrolysates whose yields were both 50% could be very different depending on

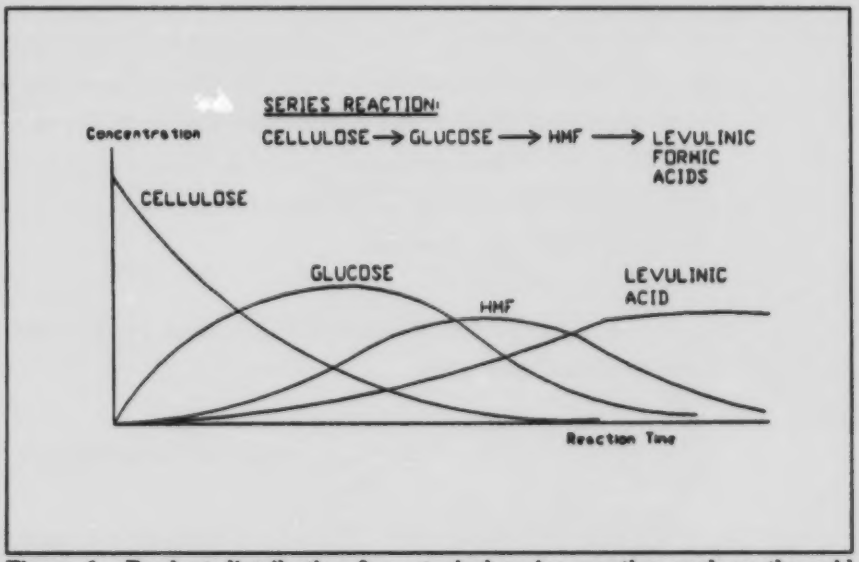


Figure 1. Product distribution for a typical series reaction such as the acid hydrolysis of cellulose.

where they lie on the glucose curve. Also, at the peak glucose concentration, the rate of production of hydroxymethyl furfural (HMF) is at its highest. Thus, there are pitfalls to going even just slightly beyond the optimum reaction time. Given the inhibitory effects of HMF and levulinic acid on the yeast, it may be wise to stay just below the optimum reaction time.

Grethlein and Converse (1982) used the following equations to define k_1 and k_2:

$$k_1 = P_1 * C^m * \exp(-E_1/RT)$$
$$k_2 = P_2 * C^n * \exp(-E_2/RT)$$

where C is the weight % of acid in the water used in the slurry. The kinetic parameters include the pre-exponential factors P_1 and P_2, the powers on the acid concentration m and n, and the activation energies E_1 and E_2.

Various plots of glucose yield versus reaction parameters were generated using the integrated material balance equations above. The kinetic parameters determined by Grethlein and Converse for white pine were used, along with the acid concentrations, temperatures, and residence times typically run in the pilot plug flow reactor. The values used were:

$P_1=7.8\times10^{13}$	m=0.963	E_1=30,170
$P_2=3.96\times10^{9}$	n=0.569	E_2=21,000

The plots of glucose yield (cellulose conversion to glucose or glucose produced/maximum available glucose) versus residence time, at constant acid concentration with temperature as a parameter, are shown in Figures 2 to 4. It is evident from the three graphs that optimum conversions of 40-50% (cellulose to glucose)

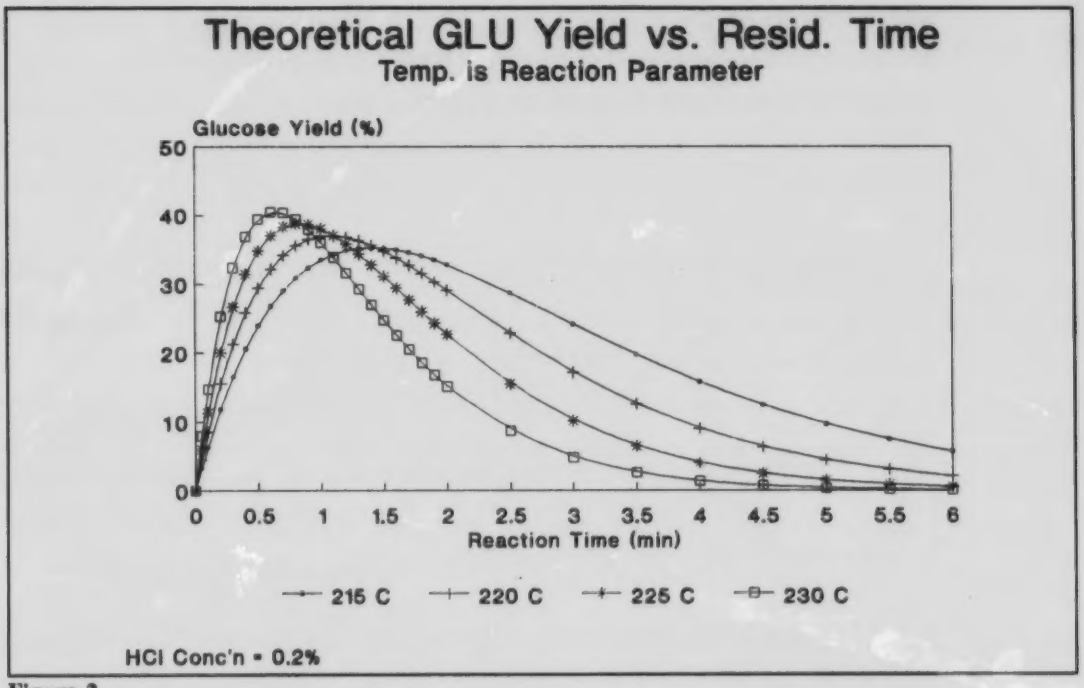


Figure 2

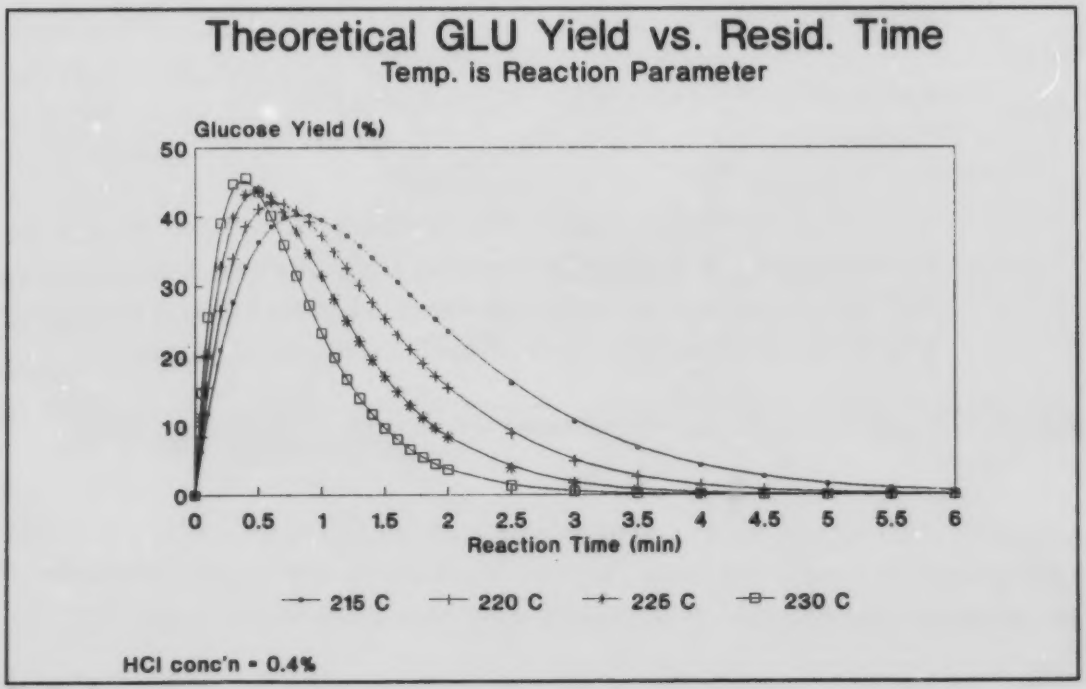


Figure 3

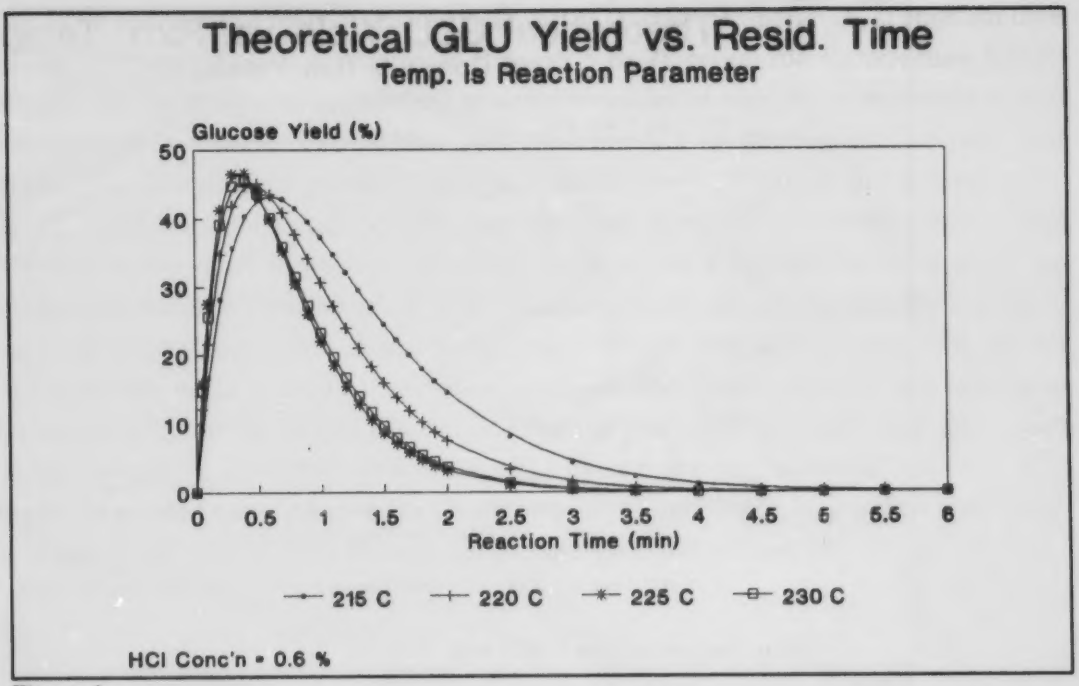


Figure 4

are possible and that, for a given acid concentration, the magnitude of these optima are increased by operating at higher temperatures (225-230°C) with shorter residence times (30 seconds or less). This is in keeping with the theory that one can increase the relative rate of the first reaction by operating at higher temperatures due to its higher activation energy. At low acid concentrations, the peaks are quite broad and not as sensitive to residence time. This is especially true at low reaction temperatures. Sharper peaks occur for higher temperatures, particularly as the acid concentration increases. As the acid concentration increases, the maximum achievable yield increases and temperature has less of an effect on yield. For example, with 0.6% HCl (Figure 4), the curves representing the different temperatures become compressed together (e.g., the 225°C and 230°C curves practically coincide). Thus, there is a limit to which one can increase both temperature and acid (and thus, increase both rate constants k_1 and k_2) and expect a greater yield. The only thing these increases achieve are to decrease the residual cellulose level and increase the concentration of breakdown products (making the product less fermentable) without an accompanying improvement in glucose yield.

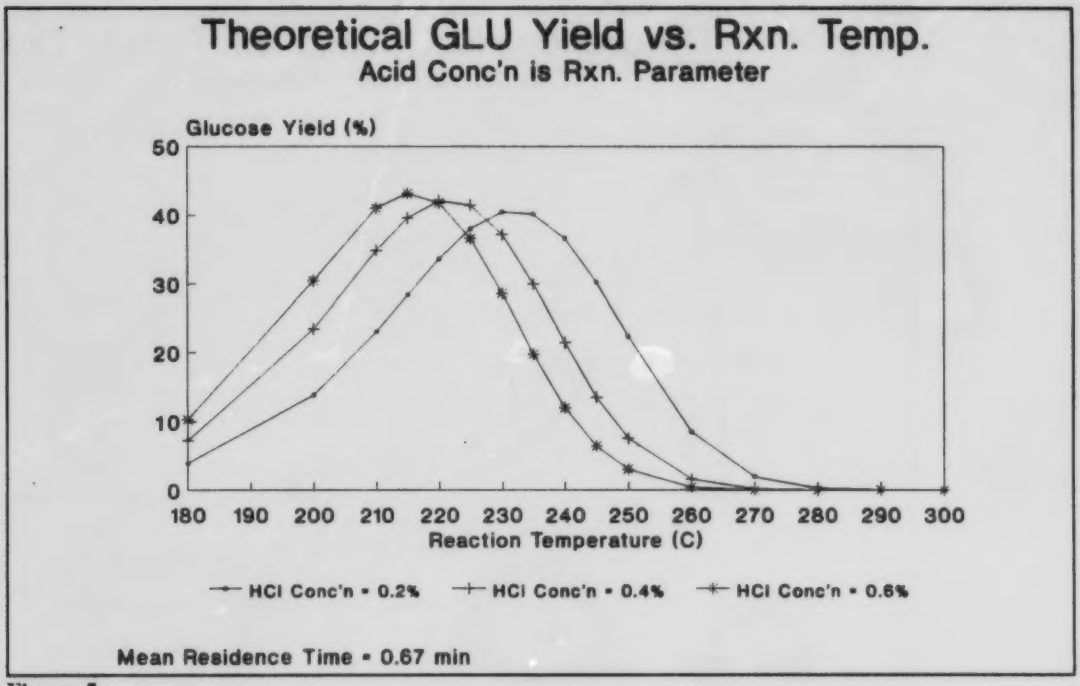


Figure 5

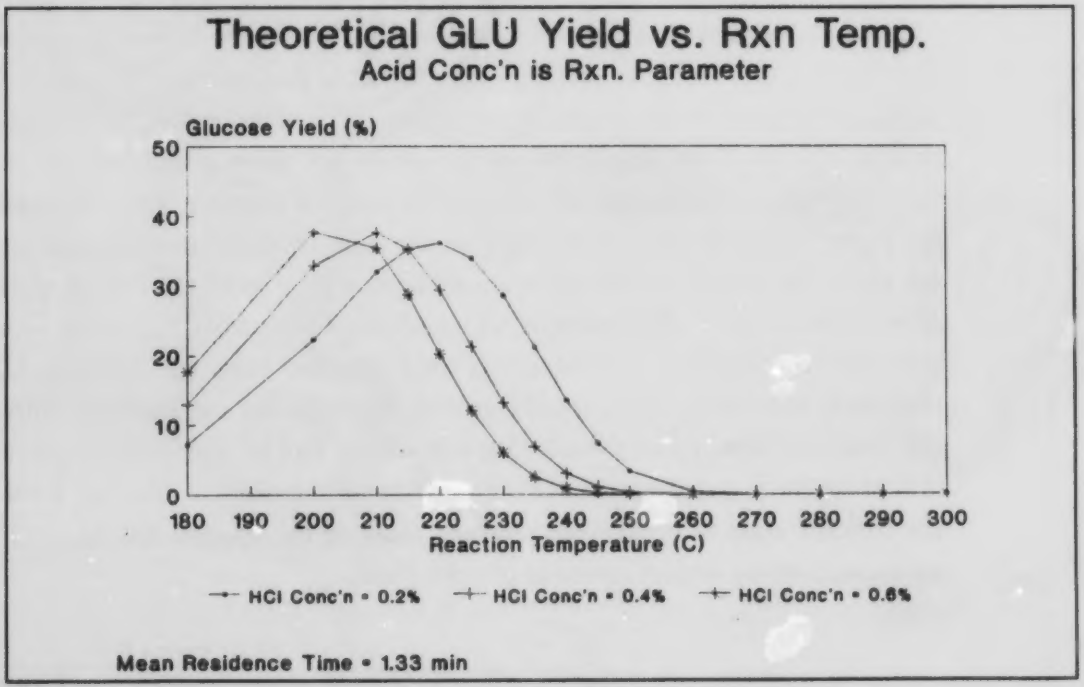


Figure 6

The comparative plots of glucose yield versus reaction temperature, at constant time with acid concentration as a parameter (Figures 5 to 7), reveal some interesting trends. As expected, the temperature required to achieve maximum conversion decreases as acid concentration increases. Thus, either acid concentration or temperature, or both, can increase the glucose yield provided there is a corresponding decrease in residence time. Slightly higher optima occur for the high acid/low temperature combinations. This difference is too small to warrant operating at the higher acid concentrations given the likelihood of increased toxicity to the yeast. It is particularly noteworthy that the maximum attainable yield drops quite dramatically, regardless of temperature and acid, as the residence time increases. This observation reinforces the critical role that residence time plays in determining the extent of reaction once the rate constants have been established (i.e., by temperature and acid concentration). Even if the rate constants are such as to favour the production of glucose (i.e., high temperature), if the residence time is too long, the reaction will proceed too far and the glucose yield will be low.

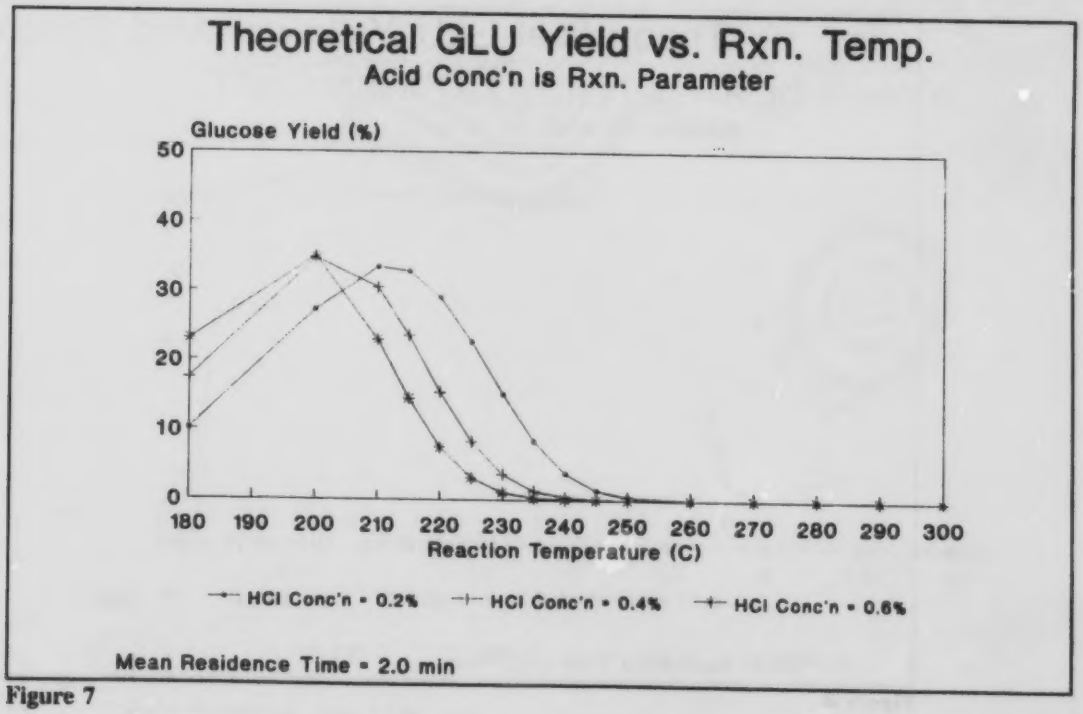


Figure 7

The plots of glucose yield versus acid concentration (Figures 8 to 11) again show the importance of having a low residence time if maximum yields are to be achieved. In addition, note how much sharper the curves are (i.e., more sensitive to acid) as time increases. With a residence time of 0.25 minutes (Figure 8), the maximum yield is over 50% and each temperature curve has a peak which is a plateau stretching across a relatively wide range of acid concentrations. This can be compared to the plot for a residence time of 2 minutes (Figure 11) which has maxima in the range of 30-35% with very little tolerance to the acid concentration. In order to achieve maximum yields (i.e., short residence time, high temperature), higher acid concentrations than the ones we have been using are called for (i.e., 0.6-1.2% HCl for a 0.25 minute residence time at 230°C). These high acid conditions may in fact present a toxicity problem but should be tested if the very high temperature, short residence time runs can be performed.

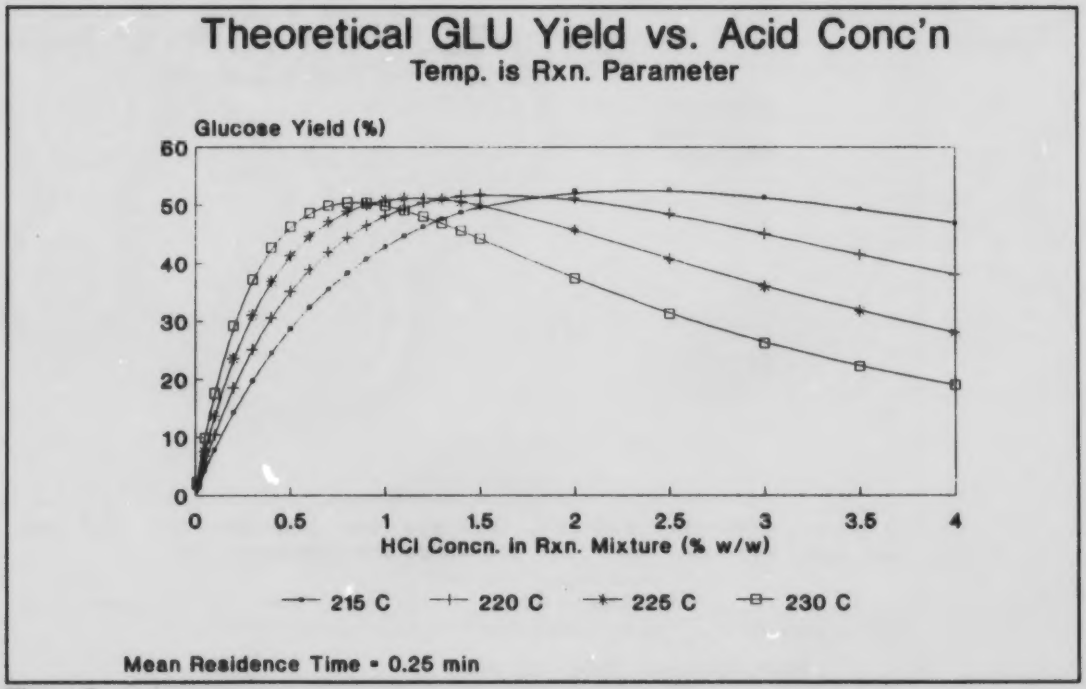


Figure 8

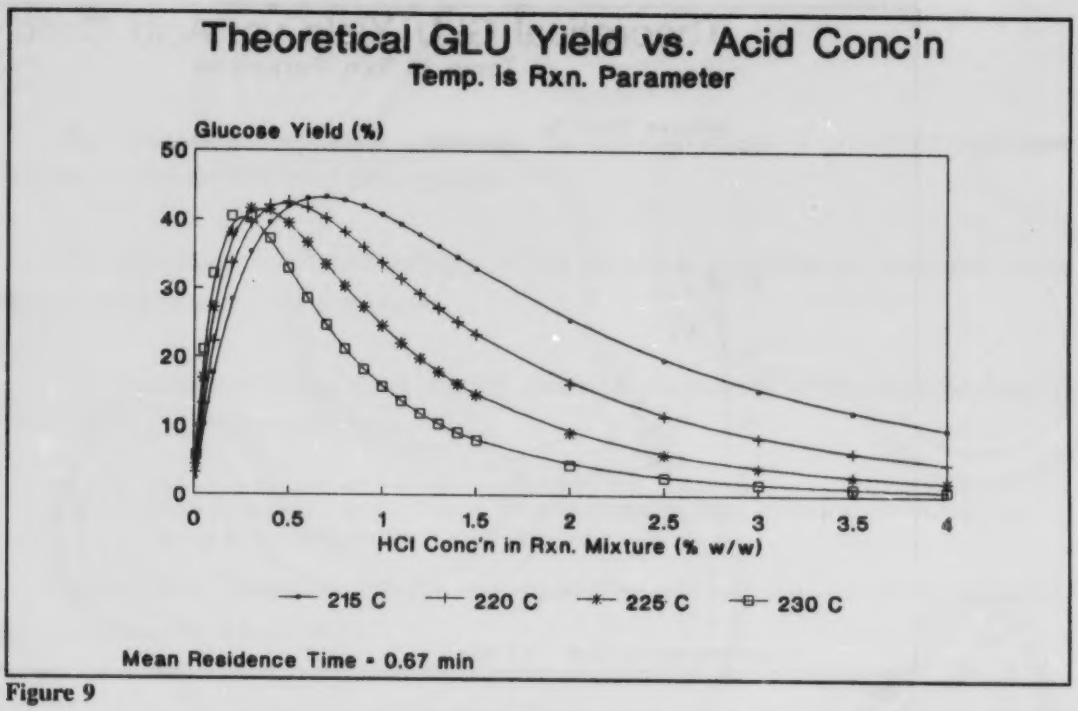


Figure 9

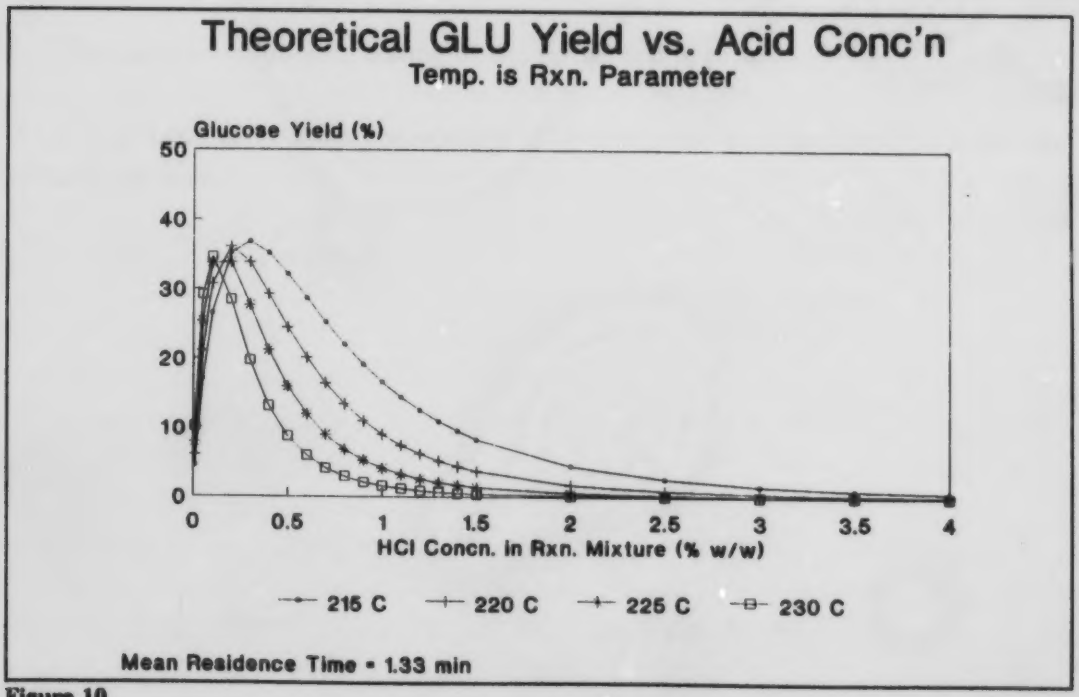


Figure 10

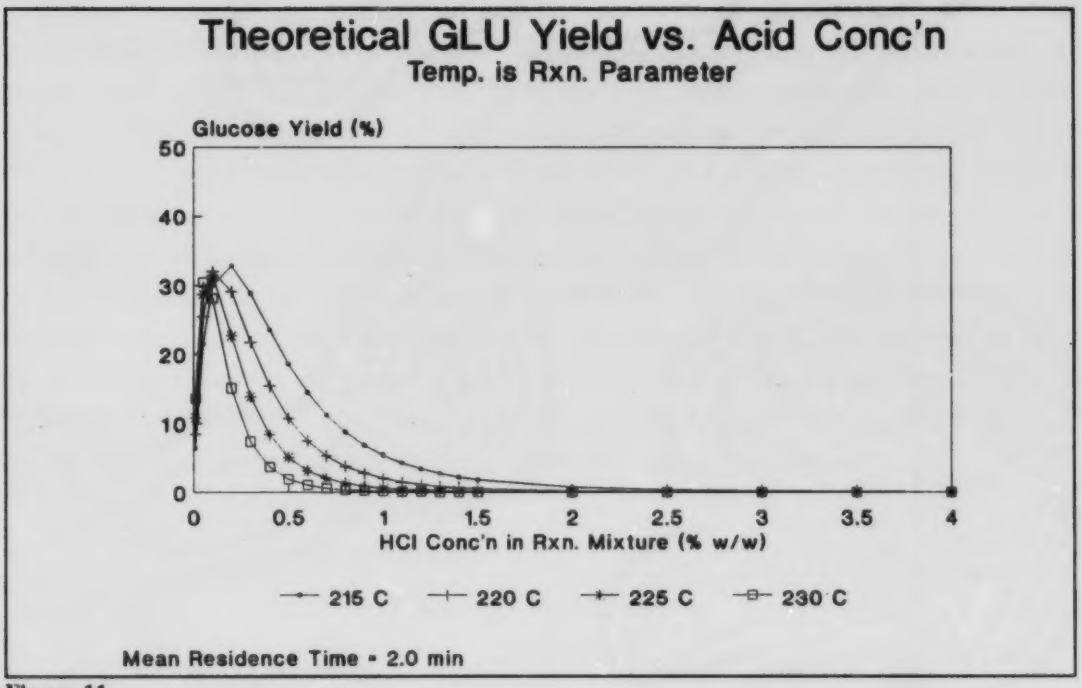

Theoretical GLU Yield vs. Acid Conc'n
Temp. is Rxn. Parameter
Glucose Yield (%)
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
3
3.5
4
HCl Conc'n in Rxn. Mixture (% w/w)
215 C
220 C
225 C
230 C
Mean Residence Time = 2.0 min

Figure 11

2. OBJECTIVES

To establish the optimum conditions for the conversion of pre-hydrolyzed pine cellulose to glucose in a plug flow reactor.

To determine the fermentability of the cellulose hydrolysates produced using different plug flow reactor conditions.

To determine whether there are any clean-up procedures which could be used to render the hydrolysates more fermentable.

To develop improved yeast strains for the fermentation of wood hydrolysates.

To carry out batch fermentations on mixed hemicellulose and cellulose hydrolysates and establish some kinetic data.

To study the separation of the liquid phase from the solid residue of second stage hydrolysis.

To carry out pilot-scale testing of the fermentation process.

To perform an economic evaluation of several possible schemes of the waste pine to ethanol process.

3. MATERIALS AND METHODS

3.1 Hemicellulose Hydrolysis

Hemicellulose hydrolysis was carried out in a Sunds Defibrator at Tennessee Valley Authority (TVA, Muscle Shoals, Alabama). The conditions used were: temperature, 160°C; liquid to solids ratio, 3:1; SO_2 content, 2.5% on dry wood substance; residence time, 30 minutes.

The TVA Sunds Defibrator hydrolyzer is a vertical pressure reactor (a schematic of the CASH process pre-hydrolysis reactor, which operates by a similar principle, is shown in Process Flow Diagram (PFD) 1-351-13 in Section 8.2). It was constructed from zirconium so that experiments with a wide range of catalyst acids (stainless steel is satisfactory for the CASH process) could be conducted. The unit has a feed hopper and hopper screw, an inlet screw feeder, impregnation screws, a bottom sweep agitator, and a pair of outlet pressure lock reciprocating valves. During operation, wood substance is introduced into the feed hopper at a predetermined, fixed rate. The hopper screw feeds the main inlet screw feeder. The speed of the hopper feed screw is automatically varied as necessary to maintain a chip level in the hopper. The main inlet screw introduces the feed in a positive manner against a blow-back valve. This valve will close if the feed is interrupted (to prevent reactor blow-back through an empty feed system). Upon passing the blow-back valve, the feed enters the built-in twin-screw impregnator. A high-pressure liquid injection pump introduces water/catalyst at the beginning of the impregnation zone. As the wood substance is conveyed upward, it is thoroughly mixed with the water and catalyst (SO_2 for the CASH process). The mixture flows over the impregnator outlet weir into the reactor vessel. The reaction mass moves downward at a rate determined by the residence time required. The residence time is controlled by setting the feed rate into the reactor and then controlling the level in the reactor. The level is measured by means of a gamma guage. The level is maintained according to the cycle time of the reciprocating product-discharge valves. A further description of the hemicellulose hydrolysis process, using the Sunds Defibrator, is given by Westmoreland *et al.* (1988).

The substrate for the cellulose hydrolysis process was prepared from the residue of this hemicellulose hydrolysis by washing with fresh water, in a ratio of about 20 parts water to 1 part solid, in order to remove most of the sugar and residual acid. The washing of

the residue was performed in an open-top stainless steel tank equipped with an agitator with a three horsepower motor. The tank outlet was connected to a diaphragm pump and the pump discharge connected to a filter press header. For each batch to be washed, 500 US gallons of water was placed in the tank, about 400 pounds of wet residue was added, and mixed for 30 minutes. The slurry was then pumped to the filter press and the cake was dried with compressed air for at least 30 minutes after filtration.

3.2 Cellulose Hydrolysis

3.2.1 Description of Reactor System and Operating Procedure

The experimental St. Lawrence Reactors plug flow reactor (PFR) consisted of four triple pass (40 feet per pass) heat exchangers with a 1 inch tube diameter. The first two heat exchanger shells were supplied with 100 psig steam to preheat the feed slurry to approximately 160°C. The third shell was supplied with high pressure steam (300-450 psig) to bring the slurry to reaction temperature (215-230°C). A schematic diagram of the plug flow reactor can be found in Figure 12.

At the beginning of the project, the entire amount of acid required for the hydrolysis of the cellulose was added to the feed before it was introduced into the PFR. However, such a scheme did not permit precise control of the point at which the hydrolysis reaction actually commenced. Due to the heterogeneous nature of cellulose (i.e., occurs in both amorphous and crystalline forms), and the fact that the acid was present in the reaction mixture during heat-up, it was possible that some of the cellulose was hydrolyzed during this transient period before the final reaction temperature was reached. Therefore, in order to minimize the potential for production of fermentation inhibitors (from the sugars which could be formed during heat-up), and to allow more precise control of when the reaction commenced (and hence, the reaction time), an acid-injection manifold and an in-line static mixer were installed after the third shell (at the start of the reaction zone). It was here that 17% (w/w) HCl was injected, using a diaphragm pump (Hydroflo Cheminjector-D Series 1000), at a flow rate which provided the proper acid/wood ratio or pH. Thus, the acid was injected once the feed had reached reaction temperature, and the cellulose hydrolysis reaction was initiated at this point.

The fourth heat exchanger shell was not supplied with steam but rather served as a retention zone. The residence time was varied by changing the number of 40 foot passes through which the reaction mixture flowed (the flow rate could also be used to vary residence time). In order that the reaction could proceed at steady state and at the desired temperature, the pressure within the reactor had to be maintained at a level which was at least as high as the equilibrium vapour pressure of water at the reaction temperature. This was achieved with a restriction device (orifice) placed at the discharge end of the reactor.

For each experimental run, the necessary quantity of TVA prehydrolyzed pine was weighed into the reactor feed tank, along with the proper quantity of water, to produce a feed slurry of the desired solid concentration (usually 20% dry solids). The solids were kept in suspension by a ribbon blender within the feed tank. The normal batch sizes were between 140 and 375 kg. During the initial phases of the project, some acid was added to the feed slurry in order to decrease its pH to approximately 2.2-2.3 (It was previously determined that no significant cellulose-to-glucose hydrolysis takes place at this pH). The remainder of the acid was introduced via the injection pump. As the project proceeded, it was found that the initial dose of acid in the feed tank was unnecessary.

The feed tank was situated over the "open throat" intake of the feed pump. The feed pump was an 8-stage progressive cavity Moineau type pump (Netzsch Model No. NE60A/8N30) capable of delivering flows up to 6 USGPM at discharge pressures up to 800 psig. The normal operating flow rates were between 7 and 11 kg/min. The reactor startup procedure consisted of heating the reactor up to the desired temperature with water, from an in-line auxiliary water pump, flowing through the tubes. Once the desired temperature was achieved (controlled by adjusting the boiler pressure set point), the wood slurry was immediately fed to the reactor. Samples of hydrolysis product were collected from the discharge end of the reactor. These samples were analyzed to determine cellulose conversion and were tested for fermentability. The reactor was shut down by pumping water through the tubes (100 psig steam still on the shell side) until there was clean water exiting. The steam was then shut off and water was pumped through the reactor until it had cooled down. Periodically, the reactor tubes were cleaned using an alkaline cleaning solution (Kert Chemicals Klean-All).

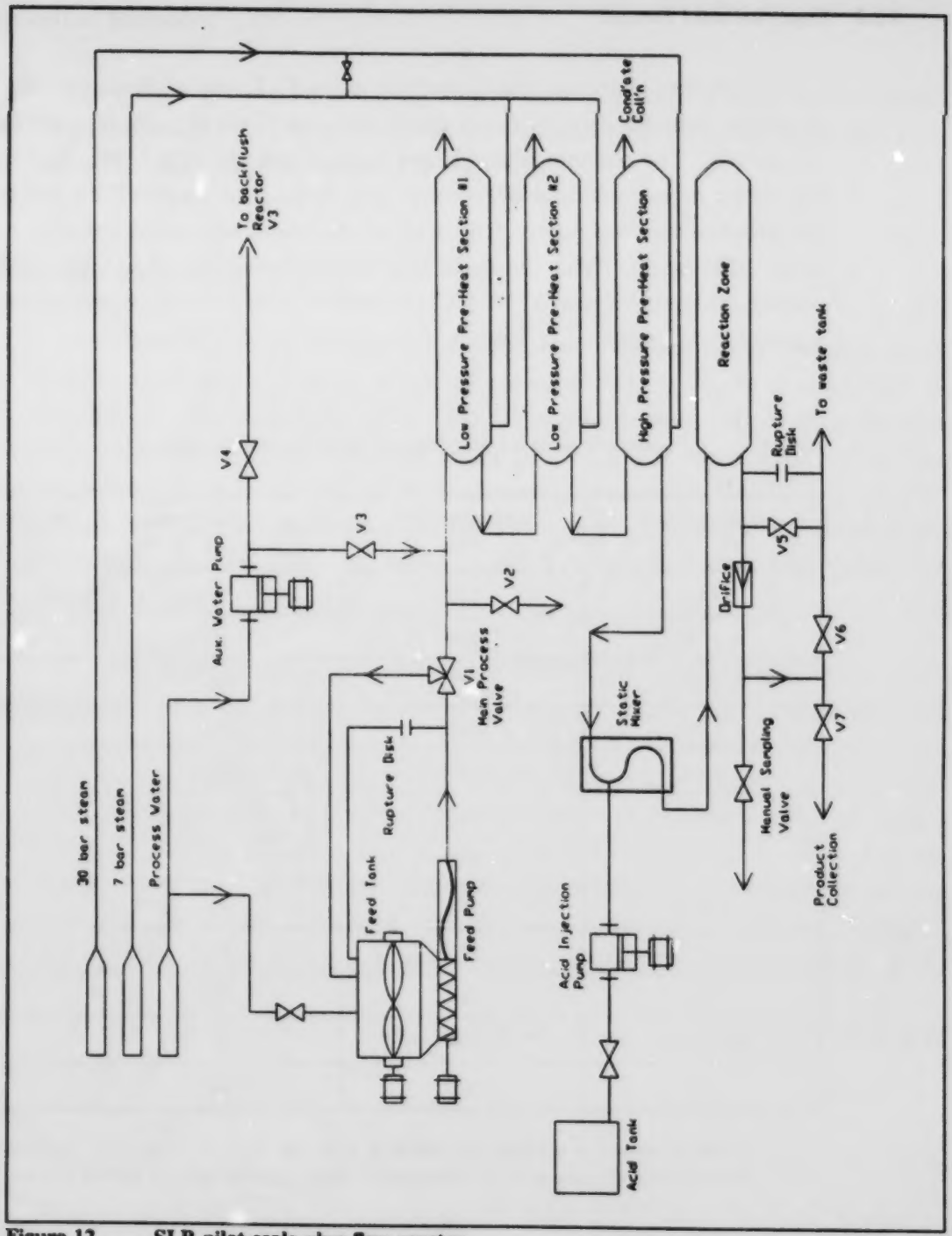


Figure 12 . SLR pilot-scale plug flow reactor.

3.2.2 Experimental Design

Cellulose hydrolysis was carried out in the St. Lawrence Reactors plug flow reactor at various temperatures, residence times, and acid-to-wood ratios (or acid concentrations in solution). The reaction temperatures ranged from 215°C to 230°C. The residence time was varied between 40 and 240 seconds by adjusting the length of the reaction zone and the speed of the feed pump. The acid-to-wood ratio was varied between 1 and 3% (dry solids (DS) basis). With the usual feed solids content of 20%, these acid/wood ratios correspond to 0.25% and 0.75% HCl in solution. The series of reactor conditions used as a guideline are outlined in Table 1.

Table 1. Conditions Used for the Determination of Reactor Conditions.

RUN NUMBER*	TEMPERATURE (°C)	REACTION TIME (sec)	ACID TO WOOD RATIO (% DS)
1 (1)	215	40	1
2 (a)	225	40	1
3 (b)	215	120	1
4 (ab)	225	120	1
5 (c)	215	40	3
6 (ac)	225	40	3
7 (bc)	215	120	3
8 (abc)	225	120	3
9	220	80	2
10	220	80	2
11	220	80	2
12	220	80	2

* If letter(s) appears in brackets, the variable is at its high level; a=temperature, b=residence time; c=acid concentration. (1) represents the experiment in which all of the variables were at their low levels.

3.3 Analytical Methods

The analytical procedures and equipment used to determine sugar concentrations (and cellulose conversions), ethanol concentrations, total and suspended solids, and acid-insoluble (Klason) lignin are described in Appendix A.

3.4 Separation methodology

Hydrolysates were neutralized before separation, using sodium hydroxide, in order to minimize equipment corrosion. Work completed during the course of the project at TVA indicated that magnesium oxide (MgO) would provide some advantages in minimizing salt toxicity during the fermentation process, and it was therefore used from that point forward. A Westphalia scroll-type decanter (Model No. CA220-010) was used to separate the aqueous stream from the finely dispersed cellulose/lignin residue of the second stage hydrolysis. This was done routinely to produce clear hydrolysates for fermentation testing.

A series of separation experiments were carried out using the scroll decanter which was fed with a Moineau pump. The feed slurry was thoroughly mixed with a propeller mixer and could be heated with indirect steam, if required. All experiments were carried out using the product from plug flow reactor run 3G (an extended reactor run at "optimal" reaction conditions). A factorial matrix of 16 experiments examined the effect of changes in feed dry solids, feed flow rate, feed temperature, and the presence or absence of the flocculating agent Berocell 439 (Berol Industries, Sweden) on both the sugar recovery in the "overs" stream and the suspended solids recovery in the "unders" stream. Statistical analysis of the results was carried out using a factorial method (Walpole and Myers, 1978).

Routine sample analyses included total dry solids and suspended solids for each of the feed, "overs", and "unders" streams.

3.5 Fermentation Testing

3.5.1 Preparation of Hydrolysate Samples

Products of the second stage hydrolysis were diluted and passed through the horizontal scroll decanter to separate the hydrolysate solution from the unreacted residue (cellulose/lignin). Having undergone a dilution as part of the washing procedure, the decantate typically had a glucose concentration of 2.5 to 3.5 %. Thus, the hydrolysates had to be concentrated in order that their fermentability (or degree of inhibition) could be assessed at various sugar concentrations. The clarified hydrolysates were concentrated to 10-20% glucose using an Alfa-Laval Centritherm CT-1B pilot-scale vacuum evaporator. The usual evaporation conditions were a vacuum of 88-91 kPa, an inlet temperature of 70-75°C, and an outlet (concentrate) temperature of 45-50°C.

3.5.2 Strain Comparison and Acclimatization

Several strains of microorganisms were compared for their ability to ferment hemicellulose and cellulose hydrolysates. The more promising strains (those able to grow and ferment at higher levels of the hydrolysates) were acclimatized to cellulose hydrolysate using gradient plates containing from 4 to 10% cellulose hydrolysate sugars by successive transfers (Braun, 1965). The gradients were prepared using a medium containing 4% fermentable cellulose hydrolysate sugars in the bottom wedge layer, and 10% in the top layer. The bottom layer was supplemented with 6% glucose to provide constant fermentable sugar concentrations throughout (i.e., 10% total). Yeast extract (Difco, 0.5%) was added to both layers. Following gradient preparation, the sterile plates were placed in a 30°C incubator for 24 hours to alow the formation of diffusion gradients containing the soluble cellulose hydrolysate-derived inhibitors. Freshly grown cells of each test strain were streaked across the gradient plates in the direction of the increasing gradient. After 48 hours incubation at 30°C, the relative growth tolerances and acclimatization rates of the strains were determined by measuring the length of developed streaks on the plates. Cells from the farthest end of the streak (closest to the higher concentration of hydrolysate) were then picked and re-streaked in the same manner on a fresh gradient plate. This process was repeated for a total of five passes. The acclimatized strains obtained in this manner have been maintained on gradient plates throughout the study.

3.5.3 Effective Inhibitory Concentration (EC_{50}) Testing

EC_{50} values were determined by measuring weight loss (due to CO_2 generation) over time for various concentrations of the cellulose hydrolysates. Tests were carried out in duplicate in test tubes at 30°C with no agitation or aeration. The EC_{50} was defined as the sugar concentration of the hydrolysate which resulted in a 50% reduction of fermentative activity as compared to the non-hydrolysate (pure glucose) control. Uninoculated controls were used to correct for evaporative losses during the EC_{50} determinations.

3.5.4 Batch Fermentations

Lab-scale batch fermentations were carried out in MultiGen fermenters (New Brunswick Scientific, Edison, NJ) with a working volume of 1 litre. The fermentation temperature was 30°C, the agitation rate was 240 rpm (three Rushton impellers), the aeration rate was 0.05 volume/volume/minute (vvm), and the pH was controlled at 5.5. These settings were chosen based on previous experience with *Saccharomyces cerevisiae* fermentations. Exhaust gases from the fermentation were passed through a water cooled condenser to minimize evaporative losses of ethanol. Samples were aseptically removed periodically and tested for sugar and ethanol concentration, and biomass content (by cell count or OD_{620} measurement).

Batch fermentations were carried out using either cellulose hydrolysate or mixed cellulose/hemicellulose hydrolysates as the feedstock. The concentration of fermentable sugars to be used in each feedstock was based on the EC_{50} value determined for the particular batch of hydrolysate used. Yeast extract (Difco, 0.5%) was added to all fermentations. Control fermentations were conducted using a mixture of pure sugars (glucose, mannose, galactose, arabinose, and xylose) at concentrations comparable to those actually measured in the hydrolysates. These controls were included to determine the maximum fermentation activity obtainable in a medium free of wood-derived fermentation inhibitors.

Large-scale batch fermentations were carried out in an IF-250 fermenter (New Brunswick Scientific, Edison, NJ) with a working volume of 100 litres, temperature of 30°C, pH of 5.5, agitation at 100 rpm, and aeration at 0.1 vvm. The fermentation medium consisted of a 50:50 mixture of hemicellulose hydrolysate (50-60 g/L fermentable sugar, as

received from TVA), cellulose hydrolysate (50-60 g/L glucose, based on the determined EC_{50} value of the batch being used), and 0.5% yeast extract.

3.5.5 Clean-up Procedures

The hemicellulose hydrolysate produced by TVA was treated at Bio-hol by passing through the St. Lawrence Reactors plug flow reactor at 160°C with a residence time of approximately 3 minutes. This treatment was done in order to simulate the flashing of volatiles and steam which would occur in the proposed production facility.

Over-liming (CaO) and sulphite treatment was carried out as described by Leonard and Hajny (1945). The treatment consisted of increasing the pH of the hydrolysate to between 10.0 and 10.5 by the addition of CaO, addition of 1 g/L of sodium sulphite, heating at 90°C for 30 minutes, neutralizing to pH of 7 to 7.5, followed by filtration through Whatman #1 filter paper or equivalent. This material was then used in fermentation studies.

4. HYDROLYSIS RESULTS

4.1 First Stage Hydrolysis at TVA

4.1.1 Feedstock Composition

Various sources of pine (Swedish - *Pinus sylvestis*, US - *Pinus treda*, Canadian - *Pinus banksiana*) were analyzed by the Tennessee Valley Authority (TVA) to establish whether species differences existed. The compositions shown in Table 2 were surprisingly similar, considering the diversity of the sources. The Swedish sample was taken to be representative of a typical middle-European pine.

Table 2. **Compositional Analysis of Selected Pine Samples[a]**
(presented by R. Westmoreland (TVA))

Component	U.S. Pine	Canadian	Swedish	Fuel Chips
Extractives(total)	4.28	4.24	5.10	10.70
a) Toluene/ethanol	4.28	4.24	5.10	8.57
b) Cold water	ND	ND	ND	2.13
Carbohydrate(total)	60.42	62.41	61.57	50.25
Glucan	41.09	41.97	40.65	32.55
Mannan	9.91	10.43	10.50	7.24
Galactan	2.84	2.76	2.82	3.46
Xylan	5.06	5.48	5.76	4.40
Arabinan	1.52	1.77	1.84	2.60
Lignin (total)	28.58	27.68	26.38	28.48
Klason	27.70	26.74	25.60	27.51
Acid soluble	0.88	0.94	0.78	0.97
Ash	0.37	0.22	0.26	1.31
Acetic acid, uronic acid, others	6.36	5.45	6.68	9.26
TOTAL	100.0	100.0	100.0	100.0

a compositions listed are percent by weight (bone dry basis)
ND not detected

The composition of Swedish "fuel chips" is included in the table. These were proposed by the Swedish Ethanol Development Foundation (SEDF) as an alternate feedstock for the process. It is a low-grade feed material which is composed of trimmings, branches, needles, leaves, bark, and off-spec chips from various species (both hardwood and softwood). This material has no practical value other than as a hog fuel. The presence of hardwood and needles and leaves was indicated by the higher level of acetyl groups, and extractives/ash, respectively.

4.1.2 Hemicellulose Hydrolysis

The production of hemicellulose hydrolysate was carried out in a Sunds Defibrator, using Swedish pine as feedstock. Sulphurous acid, prepared as a solution of SO_2 in water, was the prehydrolysis catalyst. TVA had optimized the prehydrolysis reactor conditions in previous projects. The reaction temperature was 160°C, the liquid-to-solid ratio was 3:1, the acid-to-wood ratio was 2.5%, and the residence time was 30 minutes. Under these conditions, approximately 34% of the dry wood substance was solubilized, with conversion of up to 90% of the hemicellulose to its component sugars. For the pine feedstock, approximately 65% of these sugars were fermentable hexoses with the remainder being pentoses. Table 3 shows an analysis of a typical hemicellulose hydrolysate.

Table 3. Typical Concentrations and Yields of Hemicellulose Hydrolysate Products

Component	Concentration in Hydrolysate (% w/v)	Yield (% of dry matter)
Glucose	1.97	5.9
Mannose	3.01	9.0
Galactose	0.57	1.7
Total Hexoses	5.56	16.6
Xylose	1.61	4.8
Arabinose	0.41	1.2
Total Pentoses	2.02	6.0
Total Sugars	7.78	22.6
Furfural	0.1	0.3
HMF	0.1	0.3
Acetic Acid	0.45	1.4

4.2 Cellulose Hydrolysis

4.2.1 Composition of TVA Prehydrolysis Residue (2nd Stage Feedstock)

The residual solid from TVA's prehydrolysis of pine was shipped to Bio-hol for second stage (cellulose) hydrolysis tests. TVA's hydrolysis conditions were well established and resulted in products which were fairly consistent in composition. The moisture content was usually on the order of 60%. On a dry basis, the typical composition of the prehydrolysis residue was 50% cellulose, 44% lignin, and 6% "others" (e.g., insoluble ash, hydrophobic extractives, etc.).

4.2.2 Optimization of Reactor Operating Conditions

The choice of reaction conditions for the dilute acid hydrolysis of the cellulose fraction depended not only on glucose yield but on hydrolysate fermentability as well. Conditions which provide optimum conversion of cellulose to glucose may prove to be completely unsuitable from the standpoint of fermentability. Due to the nature of the reaction, a low glucose yield does not necessarily suggest a "mild" hydrolysis and a fermentable substrate. Two runs which have the same measured glucose yield may actually fall on opposite sides of the peak glucose production and thus differ greatly with respect to the extent of cellulose reaction (see Introduction, Section 1.7). Runs 2B and 3D (Table 4) are examples of such a phenomenon. Run 2B showed a low cellulose-to-glucose conversion but was very fermentable. Run 3D had a similar cellulose-to-glucose conversion but much higher levels of inhibitory degradation products.

It is well established that glucose dehydration products such as hydroxymethyl furfural and levulinic acid act as inhibitors in fermentation processes (Faber *et al.*, 1982). Thus, unless these substances can be removed from the hydrolysate and collected as co-products, the hydrolysis conditions should be controlled in order to minimize their production relative to glucose. The choice of harsh hydrolysis conditions followed by a "clean-up" of the resulting hydrolysate would mean an increased degree of solubilization of the feed, and proportionally less of the cellulose/lignin residue would be available for use as a boiler fuel. In addition, "clean-up" processing would involve higher operating and capital costs. Thus, it is preferable to stay on the "mild" side of the optimum glucose production conditions. An appropriate statistic to consider, along with glucose yield and

fermentability, would be glucose selectivity (glucose produced/cellulose reacted). This would take into account the efficiency of the hydrolysis process with respect to useable products.

4.2.2.1 Trends from Experimental Design

In examining the effect of reaction temperature, residence time, and acid concentration, on both glucose yield and hydrolysate fermentability, the basic experimental design outlined in the materials and methods section was followed. Achieving precisely the pre-set levels of the three operating parameters proved to be a difficult task. Nevertheless, the basic design was followed. The results of these runs are presented in Table 4. The complete record of cellulose hydrolysis runs is contained in Appendix B (Table B.1). A statistical evaluation of these results (cellulose-to-glucose conversion only) is also included in the appendices. (The factorial analysis served mainly to confirm trends and interactions. It should not be considered rigorous because some of the parameter values included as being at the same level were actually variable.)

Statistical analysis of the data in Table 4 (see Appendix B, Table B.2) revealed that none of the main effects (i.e., temperature (a), residence time (b), and HCl concentration (c)) were, by themselves, significant in their effect on glucose yield. The two-factor interactions of temperature-time (ab), temperature-acid (ac), and time-acid (bc) were all significant at a 5% level of significance. This was evident in that the effect of the first factor was dependent on the level of the second factor. For example, in the temperature-time (ab) interaction, the effect of temperature was positive at the low level of time (eg., Z versus 2B; 2A versus 2O). However, the effect of temperature was either negative or negligible when residence time was at its high level (eg., 3D versus R; 2C versus O). There was some evidence of a three-factor interaction; in each case, the level of the first two factors influenced the effect of the third. This influence seemed to be outweighed by the fact that the yield of the abc (high, high, high) experiment was not significantly different from that of the experiment labelled (1) (low, low, low). The similarity of glucose yield in these two extreme cases was likely due to them occurring on opposite sides of the optimum on the glucose yield curve (see Section 1.7). Statistical analysis of such complicated interactions can be difficult.

Table 4. **Hydrolysis Runs Performed to Examine Effects of Operating Conditions on Glucose Yield and Hydrolysate Fermentability**

Run	Temp (°C)	Resid. Time (min)	% HCl in soln.	GLU Conv. (%)[a]	HMF Conv. (%)[b]	LEV Conv. (%)[c]	Ferment-ability[d]
O	215	2.6	0.28	41.9	1.7	1.1	good
R	216	2.2	0.72	46.4	5.4	8.6	poor
Z	226	0.8	0.27	45.0	1.4	ND	good
2A	227	0.8	0.81	49.6	12.6	12.6	poor
2B	216	0.7	0.22	24.8	ND	ND	good
2O	215	0.7	0.62	43.7	2.6	9.2	moderate
2C	223	3.5	0.36	46.7	6.9	16.6	poor
3D	228	1.9	0.54	18.5	4.5	30.2	poor
X	220	1.5	0.51	45.5	4.4	5.1	NA
2M	221	1.4	0.44	38.5	5.3	14.6	NA
2N	218	1.3	0.43	37.1	3.6	10.1	moderate
3E	218	1.8	0.25	46.5	NA	6.5	moderate

a (Cellulose converted to GLU/Initial Cellulose) * 100%
OR (GLU Produced/Initial Cellulose)/1.11*100%

b cellulose conversion to 5-hydroxymethyl furfural (5-HMF)

c cellulose conversion to levulinic acid and formic acid

d fermentability: good = EC_{50} > 6%
moderate = 2% < EC_{50} < 6%
poor = EC_{50} < 2%

ND not detected

NA not available

It is apparent from Table 4 that the maximum cellulose conversion to glucose attainable via acid hydrolysis in the plug flow reactor was approximately 50%. This agrees quite well with theory (Section 1.7). The effect of the reaction temperature (variable "a" in statistical analysis) was particularly noticeable when the other reaction parameters were set at their "low" levels; the glucose yield increased markedly when the temperature was

increased from 216°C to 226°C (run 2B versus run Z). Conversely, when the other two factors were at their "high" levels, increasing the temperature resulted in a significantly lower yield (run R versus run 3D). With the temperature, reaction time and acid concentration set at their high levels in run 3D, the reaction appears to have proceeded far beyond the optimum glucose yield. In fact, 30% of the cellulose reacted to produce the relatively stable levulinic acid. Temperature apparently had no significant effect when either of the other factors was at the high level (eg., run O versus run 2C; run 2A versus run 2O). Evidently, with either "time" or "acid" at the high level, the glucose yield was near its peak level, and the maximum of the glucose yield curve was fairly broad and not overly sensitive to temperature.

Raising the acid concentration increased the glucose yield slightly when one of the other parameters (temperature or time) was at its high level but similarly (as occurred with temperature) resulted in a lower yield when both "temperature" and "time" were at the high level (compare runs 2C and 3D). A higher acid concentration, because both k_1 and k_2 are increased, appeared to significantly increase the production of glucose degradation products (i.e., compare run 2B to each of Z, O and 2O). This was particularly noticeable in its adverse effect on fermentability. It is not certain that this inhibitory effect of high acid concentration reflects only the elevated quantities of HMF and levulinic acid produced. It is possible that other inhibitors (e.g., polymerization products of HMF) were generated at the high acid concentrations.

Reaction time does not affect the rate constants and hence does not affect the maximum attainable glucose yield. However, it is nevertheless critical in achieving optimum yield because it controls the extent of the reaction. Theory suggests that precise control of residence time is more crucial at high reaction temperatures, especially when these are coupled with high acid concentrations (see Figures 2-4 in Section 1.7). The experimental results in Table 4 show that time had a significant negative effect on glucose yield when the other factors were already at their "high" level (run 2A versus run 3D) and a significant positive effect when the other factors were at their "low" level (run 2B versus run O). There was no significant effect on yield when only one of the other parameters was at its "high" level (run Z versus run 2C; run 2O versus run R).

Our data, in agreement with the literature (Grethlein and Converse, 1982), suggested that the potentially conflicting interests of maximizing glucose yield and

minimizing glucose degradation were best resolved at conditions of high reaction temperature, short residence time and relatively low acid concentration. These conditions were examined more closely during a series of runs aimed at reproducing the high yield and fermentability of our initial tests. The results of these runs are highlighted in the next section.

4.2.2.2 Reproducibility of Reactor Runs

The success of runs Z and 2U, both in terms of glucose yield and fermentability, was followed up with a series of repeated experiments. The results are presented in Table 5. The reaction parameters varied slightly from run to run but were, for the most part, within the range considered to be optimum. The cellulose-to-glucose conversions in these experiments ranged from 36 to 53%, with most between 40 and 45%.

Table 5. Runs Performed at Chosen Operating Conditions to Study Reproducibility and Fermentability

Run No.	Temp (°C)	Resid. Time (min)	% HCl in soln.	GLU Conv. (%)[a]	HMF Conv. (%)[b]	LEV Conv. (%)[c]	Ferment-ability[d]
Z	226	0.8	0.27	45.0	1.4	ND	good
2U	228	0.6	0.19	49.2	6.1	2.8	good
2V	229	0.5	0.18	40.3	2.0	0.6	
2W	228	0.7	0.22	52.6	8.3	1.6	
2X	230	0.6	0.23	43.7	5.5	4.0	
2Y	230	0.7	0.19	43.6	2.1	ND	good
2Z	233	0.7	0.28	50.3	6.9	3.3	moderate
3A	230	0.9	0.34	45.5	15.0	9.4	poor
3B	227	0.6	0.15	35.9	1.7	2.4	good
3F	228	0.5	0.17	44.3	4.5	2.8	moderate
3G	232	0.5	0.18	40.8	NA	NA	moderate
3H	229	0.6	0.21	48.5	NA	NA	moderate

a (Cellulose converted to GLU/Initial Cellulose) * 100%
OR (GLU Produced/Initial Cellulose)/1.11*100%

b cellulose conversion to 5-hydroxymethyl furfural (5-HMF)

c cellulose conversion to levulinic acid and formic acid

d fermentability: good = EC_{50} > 6%
moderate = 2% < EC_{50} < 6%
poor = EC_{50} < 2%

ND not detected

NA not available

A cellulose-to-degradation products conversion of 10-12% appeared to be somewhat of a threshold in terms of maintaining fermentability. The majority of these hydrolysates proved to be fermentable, but unlike those from runs 2U and Z, they were not fermentable at concentrations as high as 12% sugar. Test-tube experiments showed most of these hydrolysates to be fermentable at concentrations up to 6-8% glucose.

Given these results, it was decided that despite having 8% fermentable sugar as our original target concentration, it would be more prudent to use a mixed hydrolysate (i.e., equal portions of TVA first stage hydrolysate and Bio-hol second stage hydrolysate) at 6% fermentable sugar for our initial pilot-scale fermenter runs. Decisions whether to ferment at higher concentrations would depend on the success of these initial runs. This is discussed in more detail in Section 5.4 which describes the results of the pilot-scale fermentations.

A further implication of these results was that perhaps the "optimum" reactor conditions should be re-assessed. These could be called the optimum reaction conditions if the results of runs Z and 2U were readily duplicated. Although the glucose yields achieved were repeatable, fermentability was not. Hypotheses as to why the fermentability was not repeatable would include differences in post-reaction processing (especially degree of concentration by evaporation and its effect on the levels of volatile inhibitors) and possible changes in the yeast strain during the course of the project, despite the fact that the yeast was maintained under stringent conditions (repetition of the fermentability studies late in the project showed results consistent with those from early in the project). Therefore, hydrolysis conditions such as those of runs N (Appendix B, Table B.1) and O (Table 4), with a lower reaction temperature (215-220°C) but longer residence time (2-2.5 minutes), must be reconsidered. Both of these runs had cellulose-to-glucose conversions of over 40%, low concentrations of degradation products and good fermentability characteristics. Ultimately, the decision will be based on the economics of using a higher temperature (steam consumption and operating cost) versus those of building a reactor with a longer retention zone (higher capital expenditure).

4.2.3 Extended Reactor Runs

Extended plug flow reactor runs were performed in order to: 1) generate second stage hydrolysate product to use for separation/ washing experiments, 2) produce second stage cellulose/lignin residue for tests as boiler fuel in Sweden, and 3) produce sufficient hydrolysate for lab-scale (1 litre) and pilot-scale (100 litre) fermentations. The longer duration of these runs would also allow assessment of the operational characteristics of the reactor, particularly fouling of the reactor tubes.

The extended reactor runs were numbered 3G and 3H. Early samples of these two runs are included in Table 5. The two runs were quite similar, both in terms of operating conditions and resulting conversions. Each run generated approximately 1000 lb (450 kg) of product or approximately 750 lb of liquid at 8% glucose. In both runs, the temperature was stable at approximately 230°C for around 13 minutes and then gradually fell to approximately 220°C by the end of the run (around 60 minutes). This inability to maintain reaction temperature was reflective of our boiler design rather than the operation of the reactor.

Fouling of the reactor tubes was found to be difficult to assess, because water must be passed through the reactor as part of the shut-down procedure. As a result, the reactor tubes were partially cleaned before they could be inspected. There was no visible fouling found in the pre-heat zones of the reactor. In the reaction zone itself, there was some fouling but this seemed to be localized at fittings, restrictions, and thermocouples. Sections of smooth pipe were not fouled to any great extent. Fouling should be minimized by ensuring that the flow within the pipe is well into the turbulent flow regime, thus reducing the thickness of the laminar boundary layer. Significant fouling usually occurred when there was an interruption in the flow of material through the reactor (e.g., plugged orifice or pump failure) and the product was literally "baked" on to the pipe walls.

4.2.4 Comparison of Experimental Results with a Theoretical Model

The model described in the introduction (Section 1.7) predicted peak glucose yields which were very similar to those achieved. However, the experimental peaks appear to be much broader and are not as sensitive to reaction conditions as the model predicts. This was especially true at longer residence times and at higher acid concentrations. It appears that the yield is not as strong a function of residence time or acid concentration as was predicted by the theoretical model.

The theoretical model was included in this report mainly to describe the nature of weak acid hydrolysis of cellulose and one should not put too much emphasis upon it. However, possible reasons as to why our yields differ from the theoretical include:

- Different substrates were used (prehydrolyzed pine versus pine chips).

- Non-idealities occurred in the plug flow reactor (both in ours and the one used by Grethlein and Converse to determine the kinetic parameters); the model assumes isothermal, steady state reaction, constant density, ideal plug flow (i.e., no back-mixing).
- The fact that this work was done at the pilot-scale as opposed to the lab-scale determination of kinetic parameters by Grethlein and Converse.
- Particle-size reduction of the feed material (see Section 4.2.5.4) may have enhanced our yields.
- Inherent differences may be associated with the use of HCl as a catalyst as opposed to the model's use of H_2SO_4.
- A substance as complex as wood is very difficult to model accurately; this especially applies to the assumption that a single "effective" pseudo-first-order rate constant could be used to describe the kinetics of cellulose hydrolysis (in fact, there are likely to be a whole series of rate constants depending on the crystallinity and degree of polymerization in the various regions of cellulose).
- Analytical errors may occur in determining the cellulose content of the feed material as well as the glucose produced from it.
- It is difficult to measure and control reaction conditions as precisely as required.

4.2.5 Process Details

4.2.5.1 Acid Injection versus Addition Directly to Feed

One of the major undertakings during the early days of the project was a modification of the plug flow reactor to allow for acid injection into a feed stream which was pre-heated to reaction temperature (the equipment itself is described in Section 3.2.1). The original pilot plug flow reactor required the catalyst acid to be included in the feed tank. This meant that acid was present, along with the wood substrate, during the period in which the reaction mass was heated to the eventual reaction temperature. On the other hand, an acid injection scheme would ensure that the entire hydrolysis reaction took place at a steady state temperature (versus the transient conditions which existed as the reaction

mixture was brought up to temperature). Therefore, the hydrolysis reaction was initiated only when the acid was injected into the pre-heated wood stream. This gave precise control of the reaction time and allowed a decrease of this residence time to the very low values suggested by literature (less than 1 minute). The primary motivation behind the installation of such a system was to minimize the degradation of the sugars formed from the readily hydrolyzable regions of the cellulose (i.e., amorphous) during the hydrolysis of the less accessible regions (i.e., crystalline) of the cellulose. This sugar degradation was believed to be a significant source of potential fermentation inhibitors.

Though the acid-injection manifold was utilized for all of the runs conducted during the project, runs 2S and 2T were conducted to determine whether it was necessary to nevertheless include a small quantity of acid in the feed. In the early stages of the project it was determined that at a pH of 2.2, almost no glucose was produced in the reactor. It was decided however, that some acid should be present in the feed tank as a precautionary measure, in case the acid injection pump failed. It would also decrease the flow requirement of the acid pump. Subsequently, in run M, it was determined that 12.3% of the cellulose was converted to glucose when no acid, other than that required to bring the feed pH down to 2.2, was included. The discrepancy between this finding and the original determination of minimal conversion was likely caused by a longer residence time in the latter run (run M). Therefore, it was possible that this glucose was produced in the high pressure pre-heat section of the reactor (likely from amorphous cellulose). This glucose could then degrade to unwanted products (such as HMF and levulinic acid) in the reaction zone after the remainder of the acid was added.

Run 2S had no acid included in the feed (i.e., all of the required acid was injected via the acid pump just prior to the reaction zone), while in Run 2T sufficient acid was added to the feed to bring its pH down to 2.35 (i.e., the remainder of the acid needed to produce the same concentration as in run 2S was added via the acid pump). Table 6 shows that there was little difference between the two runs in terms of cellulose-to-glucose conversion and inhibitor formation. The question of whether to add some acid to the feed before heat-up should be answered by what best suits the overall design of the plant. All of the remaining runs were performed with no acid in the feed tank. If the feed material had a significant buffering capacity (see Section 4.2.5.7 Alternate Feedstocks) some acid would be added to the feed to overcome this initial buffering capacity. In such a case, the pH of the feed would be decreased to 2.2-2.5 with added acid.

Table 6. Runs Performed to Test the Necessity of Having Some Acid Present in the Feed

Run No.	Temp (°C)	Resid. Time (min)	% HCl in soln.	GLU Conv. (%)[a]	HMF Conv. (%)[b]	LEV Conv. (%)[c]
M	220	2.7	0.03	12.3	ND	ND
2S	219	2.6	0.26	31.4	8.5	17.8
2T	219	2.7	0.21	36.7	8.5	18.5

a (Cellulose converted to GLU/Initial Cellulose) * 100%
OR (GLU Produced/Initial Cellulose)/1.11*100%

b cellulose conversion to 5-hydroxymethyl furfural (5-HMF)

c cellulose conversion to levulinic acid and formic acid

ND not detected

4.2.5.2 Recovery of HCl/Analysis of Flash Steam

A condenser was installed to collect some of the steam which flashed off during product collection from the plug flow reactor. Such an analysis gave valuable information regarding the possibility of recovering and recycling acid (HCl) which would otherwise be lost.

A complete chloride analysis was done on run 2U (see Appendix B). This indicated how much HCl could be recovered from the flash steam, and whether some of the chloride remained in the solid residue as reacted material. A mass balance was performed to determine the feasibility of recovering HCl in the flash steam (see Appendix B for calculation). It was shown that about 99% of the injected HCl was found in the soluble portion of the product and only 0.3% of the HCl was in the flash steam. This 0.3% level agreed quite well with a theoretical flash calculation (0.4%) if it was assumed that the flash steam is at 100°C and the partial pressure of HCl at 100°C is used. Thus, it seems that recovery and recycle of flashed HCl is not practical.

4.2.5.3 Analysis of the Insoluble Residue of Second Stage Hydrolysis

Klason lignin analyses of the insoluble residue from two of the optimal reactor runs yielded some interesting results. More cellulose reacted than was originally believed or than was indicated by the cellulose-to-glucose conversions.

Run 2U, which produced a cellulose-to-glucose conversion of 49.2% (see Table 7), had an insoluble residue which was 21.1% cellulose and 77.8% lignin (dry weight basis). Based on the cellulose content of the insoluble residue, if the initial cellulose content of the feed dry solid was 50%, 71.7% of the initial cellulose was converted. However, based on the hydrolysate analysis (refer to Table 5), it was found that 58.1% of the initial cellulose was converted to glucose, HMF, & levulinic acid. Thus, 13% of the original cellulose is unaccounted for by these three measured constituents of the hydrolysate. This suggests that cellulose reacts to form compounds other than glucose, HMF, and levulinic acid. In fact, an extensive array of compounds are formed during acid hydrolysis of polysaccharides. Such reaction mixtures typically consist of hexoses and reversion products (re-polymerized sugars), HMF, levulinic and formic acids, intermediates, hydroxyacetylfuran, soluble brown polymers and insoluble black humins which are formed from HMF and its intermediates (Kuster, 1990).

Run 2W, which, based on the hydrolysate analysis, had a cellulose-to-glucose conversion of 52.6% (Table 7), had an insoluble residue which contained 16.6% cellulose and 82.4% lignin. Therefore, based on the composition of the residue, 80.2% of the initial cellulose reacted. From the analysis of the hydrolysate (Table 5), the overall cellulose conversion was determined to be 62.5%. Thus, 17.6% of the initial cellulose exists as reaction products other than the three measured compounds.

It is noteworthy that the content of lignin and residual cellulose in these samples added up to almost 100%, implying that there was very little else in the insoluble residue of second stage hydrolysis.

Table 7. Results of Second Stage Residue Analysis.

Expt. Run	Cell-to-Glu Conv.(%)[a]	% Insoluble Solid [b]	Insoluble Residue[c]		% Cellulose Conversion[d]
			% Lignin	% Cellulose	
2U	49.2	62.4	77.8	22.1	71.7
2W	52.6	58.0	82.4	16.6	80.2

a calculated based on glucose in hydrolysate
b dry basis, % of product solids that are insoluble
c dry basis, composition of washed residue
d overall cellulose conversion, calculated based on composition of residue

4.2.5.4 Effect of Particle Size of TVA Prehydrolysis Residue

It was imperative that the feed material to second stage hydrolysis was sufficiently refined to allow for pumpability at high feed solids contents (at least 20%) and to ensure that all unreacted solids could pass through the orifice. It was noticed that the TVA prehydrolyzed pine residue had some unreacted chips remaining in it. Rather than risk plugging the reactor's orifice, a grinding/refining step was inserted into our process. It should be noted that the prehydrolysis reactor in the prospective ethanol plant was designed to include a refiner. For our pilot trials, the Wenger extruder was used to reduce the particle size of the TVA pine prehydrolysis residue. The temperature during grinding reached a maximum of 100°C. Analysis confirmed that this treatment had no effect on the composition of the feed.

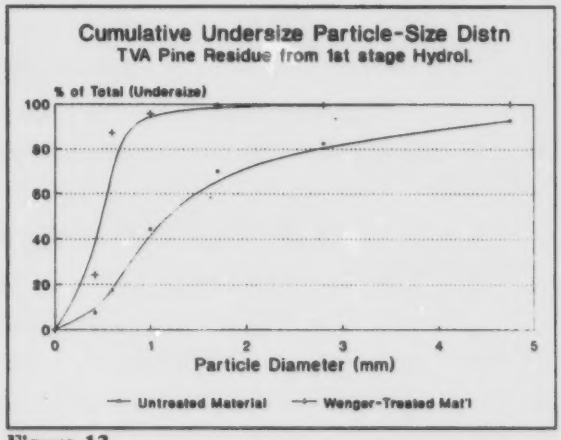


Figure 13

A particle-size distribution for both ground and unground residue is shown in Figure 13. It was speculated that perhaps refining the feed could lead to improved cellulose conversions by virtue of the cellulose fibres (and hence, the glycosidic bonds)

being rendered more accessible to acid. Grethlein and Converse (1982) point out that when the particle size of the cellulose solids is less than 20 mesh (0.84 mm), diffusion of acid or sugar are not the rate-controlling steps of the hydrolysis. Our own results did not show significant differences in glucose yield between unrefined and refined TVA residue. However, the particle-size distribution showed that approximately 90% of the treated and only 40% of the untreated particles are smaller than this proposed threshold of 0.84 mm. Thus, it is still possible that the grinding did indeed have an effect even though our results did not confirm it.

4.2.5.5 Fuel Value of the Insoluble Residue of Second Stage Hydrolysis

Processes such as enzymatic hydrolysis of wood or solvent-pulping of wood chips manage to process wood feed materials without damaging, or rendering unreactive, the lignin portion (Bungay, 1982). The lignin could then be used as a chemical reagent or precursor in the production of various plastics, resins, adhesives and other high value products. However, the structure of lignin is extensively changed during acid hydrolysis. The lignin product of acid hydrolysis is more or less condensed and can be used either as a fuel or be subjected to various treatments to yield low molecular weight degradation products including phenols. The problem with these latter products is that they are quite difficult to separate from the complex mixture of compounds formed (Sjostrom, 1981).

Therefore, the CASH process currently foresees the utilization of the lignin/cellulose residue as a fuel. In this regard, its advantages include an increased fuel value over wood itself and the fact that it contains few sulphur compounds.

The insoluble residue from second stage hydrolysis was found to consist of 77-83% lignin and 16-23% cellulose (see Section 4.2.5.3). This composition is quite dependent upon the reaction conditions chosen, with harsher conditions resulting in less residual cellulose and proportionally more lignin. If the composition is taken to be 80% lignin and 20% cellulose, based on the heats of combustion of the individual components (i.e., lignin: 25.81 GJ/tonne; cellulose: 18.818 GJ/tonne) (Wayman *et al.*, 1979), the fuel value of the residue should be approximately 24.4 GJ/tonne (dry). The value assigned to the residue is of course dictated by the price of energy (i.e., oil). With the heat of combustion of crude oil being approximately 46 GJ/tonne, the price of the residue should be 53% of the

price of oil. If the price of crude oil can be assumed to be $21 (US) per barrel (1 barrel=0.1589m³, density=870kg/m³) or $152 per tonne, the price of the lignin/cellulose should be approximately $80 (US) per tonne.

4.2.5.6 Swedish Pilot-Scale Dryer Tests

A shipment of washed (90-95% of sugar removed) second stage hydrolysis residue (at approximately 25% solids) was sent to Sweden for pilot-scale dryer tests. This dried cellulose/lignin residue is the plant co-product which will be sold as a relatively high grade fuel.

The SEDF has included, among their process options, a plant which carries out only first stage hydrolysis, produces ethanol from the sugar produced, and dries the solid residue which will then be sold as fuel. Whether the actual CASH process uses first stage hydrolysis only, or both of the hydrolysis stages, it is recommended that the residue from the last separation/washing step be dried to about 85% solid. The residue will then be sold or utilized as a powdered fuel. The residue from first stage hydrolysis could be used as fuel without requiring further drying as it will be 40-50% dry after the last roller-press washing stage. On the other hand, the residue from second stage hydrolysis needs to be dried since it exits the final centrifuge in the separation/washing series as a "pasty sludge" with dry solid content of approximately 25%.

The heat balance (i.e., steam economy) in the CASH process was carefully planned in order to keep the necessary heat and power input at a minimum. For this reason the equipment chosen to dry the hydrolysis residue was a back-pressure dryer. In such a device, the evaporated water from the residue is kept within the dryer at a certain pressure. This pressurized steam is then sent to a steam header as secondary steam because it may contain some organics contaminants from the hydrolysis residue. The secondary steam header serves other process departments such as the distillation section. The actual dryer, which consists of a number of tube and shell heat exchangers in series, is described in more detail in Section 8.6 (refer to PFD 1-351-19).

A pilot dryer manufactured by Stork Friesland Scandinavia AB was available at Chalmer University in Göteborg, Sweden. This pilot plant was built in accordance with

the dryer system included in PFD 1-351-19. Approximately 100 kg of washed residue (50% dry solids) from TVA's first stage reactor, and 500 kg of washed residue (25% dry solids) from Bio-hol's second stage reactor was sent to the pilot plant in Göteborg for testing purposes.

When this type of dryer operates under normal process conditions, the wet material (i.e., fresh feed) has to be mixed with previously dried material (i.e., recycled from dryer product stream) before being introduced into the dryer. Stork Friesland recommended that the feed should consist of approximately 50% dried, recycled material. The mixer used to blend the two components of the dryer feed was a plough-share mixer for batch operations. Because of a lack of dried material from the second stage, some of the first stage residue was dried and used as a recycle material to mix with the moist second stage sludge during start-up. The test run was divided into 8 batches which consisted of one batch for drying some first stage residue and 7 batches for drying sludge from the second stage. The procedural details are provided in Appendix B.4 (including Table B.3 which shows the design of the experiment).

Each batch of approximately 26 kg (50/50 mix of wet sludge and dried, recycled product for a combined feed solids content of around 60%) was fed to the dryer over the course of about 15 minutes. With the dryer configuration used, the solids residence time was less than 10 seconds. Nevertheless, the resultant dried product was somewhat over-dried at greater than 95% DS. The mass balance for the pilot run with the sludge from the second stage was as follows:

In: 97.4 kg (at approx. 24% DS) or approx. 23 kg dry solids (DS).
Out: 32-14=18 kg (at approx. 97% DS) or approx. 17.5 kg DS.

The difference was partially explained by spillage of the dried material and difficulties in accurately weighing the moist sludge.

Somewhat surprisingly, the second stage sludge was quite easy to mix and handle. The blending of recycled material with fresh sludge was rapid and had a low energy consumption. No lumps of unmixed fresh sludge were found after a mixing time of about one minute. After the test there were no deposits inside the dryer. The chemical oxygen demand (COD) figures for the steam condensate collected from the second stage residue

are shown below. The analysis was made on unfiltered liquid. The level of suspended solids in the condensate was also quite low for a "dusty" material such as this.

Analysis of evaporated steam condensate:

Sample		1	2
pH		6.1	5.4
COD	(mg/l)	2080	1460
Suspended solids	(mg/l)	100	72

The particle size of the dried material from batch 7 was analyzed. It was found that 80% of the particles in the powder had a diameter of less than 500 μm, while 7% were larger than 600 μm and 2% were smaller than 60 μm. These results are depicted in Figure B.1 (Appendix B.4).

4.2.5.7 Alternate Feedstocks

TVA processed "fuel chips" (i.e., a low-grade material which is composed of trimmings, branches, needles, leaves, bark, and off-spec chips from various wood species) were run through the plug flow reactor in order to examine their suitability as an alternate source of fermentable sugars. Some difficulties were encountered with this new feed, as its handling characteristics were significantly different from those of the pine.

At 17% solids content, the feed was quite thick and viscous. It exhibited a significant buffering capacity in that it took at least twice as much acid to decrease its pH to the same level as with pine. Looking at the analytical data shown in Table 2 (presented at the February 1990 meeting by Ron Westmoreland), this buffering capacity may be partially explained by the higher levels of ash and water extractables in the fuel chips as compared to the pine. Klason lignin analysis at Bio-hol revealed that the TVA treated fuel chip residue (i.e., second stage feed) contained only 32% cellulose and 59% lignin (or acid insoluble material). Thus, there was very little potential for glucose production from this

feedstock. In fact, it was not entirely dissimilar in composition from the residue of the second stage hydrolysis of pine, which is to be burnt as a fuel.

Runs 2P through 2R (Appendix B, Table B.1) were dedicated to fuel chips. The results were poor. In Runs 2P and 2Q, insufficient acid was added to produce the necessary pH for hydrolysis. There were also difficulties maintaining the boiler temperature. In Run 2R, considerable flashing of water (and the associated temperature decrease) took place within the reactor. As a result the reaction temperature was only 211-215°C. A glucose yield of only 13.9% (with a hydrolysate concentration of 16 g/L) was attained. In run 2R, only 1% of the initial acid was recovered in the condensed flash steam and 30% was recovered as HCl in the product. Thus, 69% of the HCl that was added was either unaccounted for or reacted with the dry wood substance. Because of these processing difficulties, work on this feedstock was discontinued.

4.2.6 Equipment Design Considerations

4.2.6.1 Plug Flow Reactor Orifice Diameter

The high reactor pressures (400-500 psig), necessary for operation at the preferred temperatures of 225-230°C, were achieved with the placement of a nozzle-type restriction orifice near the discharge of the plug flow reactor. At the typical experimental flow rates of approximately 10 kg/minute and with a 1 inch tube diameter, orifice throat diameters of 0.10 and 0.15 inches were used to ensure a sufficient pressure drop. The full-scale plant would certainly utilize a larger orifice due to the increased flow rates and pipe diameters. An approximate orifice diameter for the complete (base case) plant was calculated using equations derived from Bernoulli's equation (Perry *et al.*, 1984). For a pressure drop of 100 psig across the orifice, its diameter was determined to be approximately 2 cm (0.8 inches). It should be noted that this larger orifice diameter does not imply that large particles (> 5 mm) can be accommodated in the second stage hydrolysis system. The existence of such particles would limit the sugar yields attainable because mass transfer effects (i.e., transport of acid into and glucose out of the wood particles) would significantly affect rates of cellulose hydrolysis (Grethlein and Converse, 1982).

4.2.6.2 Material Selection and Corrosion/Erosion

Hydrochloric acid was the catalyst chosen for second stage hydrolysis despite its known corrosive properties with respect to most metals of construction (Perry *et al.*, 1984). Sulphuric acid would be better from a corrosion point of view but was not selected because it was imperative that the second stage residue be free of sulphur if it was to be used as a boiler fuel.

Provided that no HCl was included in the feed stream prior to acid injection, a corrosion-resistant austenitic stainless steel such as 316L could be used for the process equipment before the addition of acid. After acid injection, material selection poses a problem because of the presence of hydrochloric acid at high temperatures. Alloys such as Hastelloy B-2 have proven to be extraordinarily resistant to HCl (Perry *et al.*, 1984) and could thus be used for process equipment (e.g., flash tanks, piping, etc.) which is subjected to low concentrations of HCl. Glass-lined steel may be ideal for the acid-injection manifold, static mixer assembly, and the reaction zone of the plug flow reactor because of its resistance to HCl. Porcelain, stoneware and refractory materials offer acid-resistance. great strength, high temperature operation, and poor thermal conductivity (an advantage which would minimize heat loss in the reaction zone). The main drawback is their susceptibility to thermal shock (Perry *et al.*, 1984).

During the course of the second stage hydrolysis experiments with the plug flow reactor, it was noted that the diameter of the reactor orifice (i.e., restriction device constructed in 316L stainless steel) tended to increase with time through a combination of corrosion and erosion. Its diameter was of course crucial in maintaining the reactor pressure at or above the saturation pressure of water at the reaction temperature. Thus, when the orifice diameter grew larger than the expected 0.15 inches, flashing occurred and consequently reaction temperatures were not maintained. The orifice should therefore be constructed from similar acid-resistant refractory materials as the reaction zone.

The maintenance of the pressure within the reactor, above the saturation pressure of water at the reaction temperature, could also be achieved with a throttling valve such as a plug cock with either a venturi port or a V-shaped port (Perry *et al.*, 1984). Such a design would allow for interactive control of the reactor pressure during hydrolysis. It may again present problems relative to corrosion/erosion of the port and the associated expense of frequent replacement.

5. FERMENTATION RESULTS

5.1 Strain development

Ten strains of *Saccharomyces cerevisiae* from a variety of sources (see Table 8), *Zymomonas mobilis* ATCC 29191, and *Pichia stipitis* R, were tested for their ability to grow on hemicellulose and cellulose hydrolysates. Considerable differences in susceptibilities to inhibitors, as seen in the rates of fermentation of both hemicellulose and cellulose hydrolysates, were observed among the *S. cerevisiae* strains tested (Figures 14 and 15). The *Z. mobilis* and *Pichia* strains showed significantly poorer tolerance to cellulose hydrolysate than did any of the *S. cerevisiae* strains and were not studied further.

Table 8. ***Saccharomyces cerevisiae* strains tested**

STRAIN	SOURCE
ATCC 24680	American Type Culture Collection
ATCC 4126	American Type Culture Collection
CASH1	Diversified Research Labs
CASH2	Diversified Research Labs
DRL99	Diversified Research Labs
HSSL	Forintek
NRC 202001	National Research Council (Canada)
NRRL-Y-2034	Northern Regional Research Labs
TVA1	TVA
TVA2	TVA

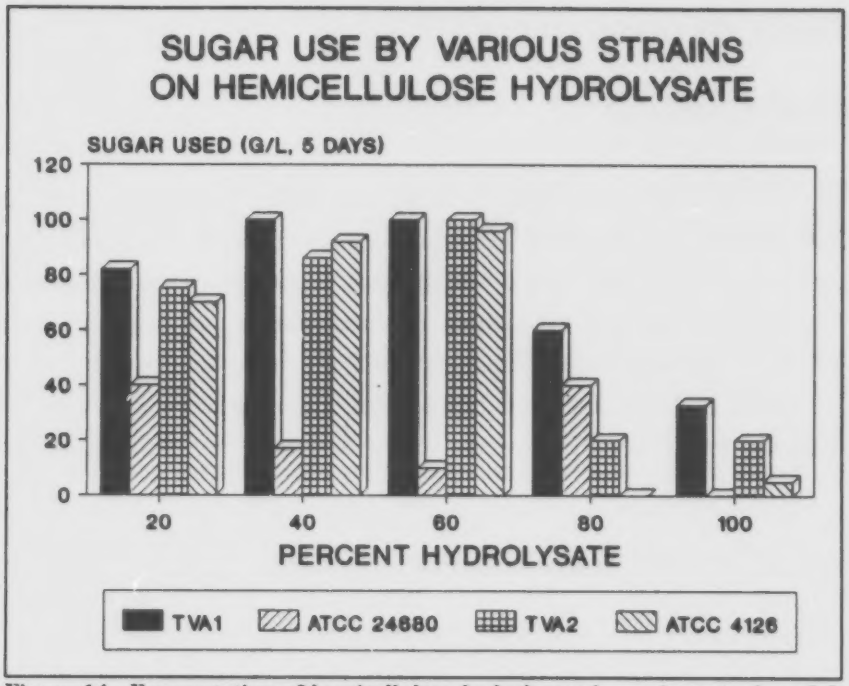


Figure 14. Fermentation of hemicellulose hydrolysate by various strains of *S. cerevisiae*

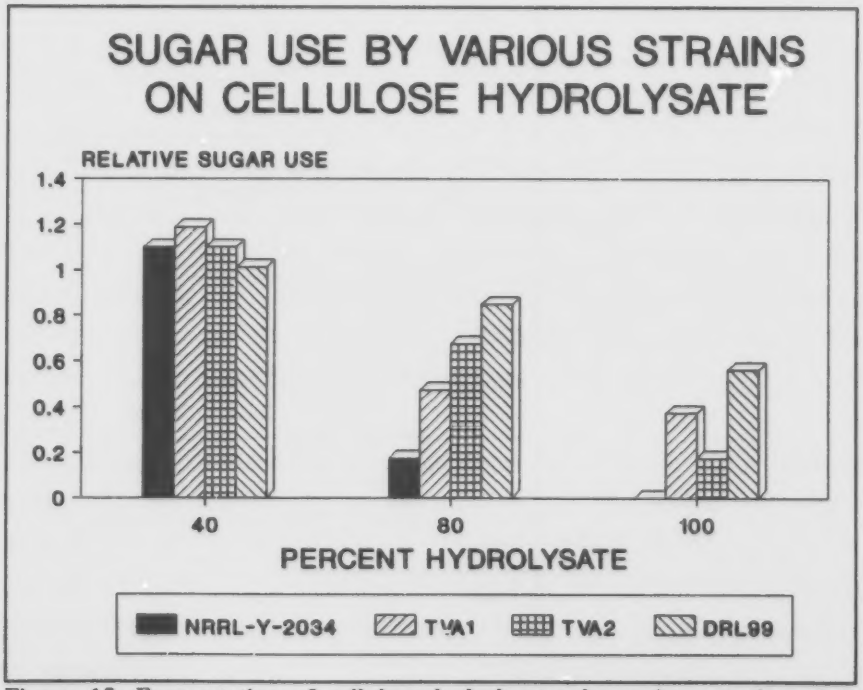


Figure 15. Fermentation of cellulose hydrolysates by various strains of *S. cerevisiae*

Differences were also found between the different *S. cerevisiae* strains tested in their ability to adapt or acclimatize to growth and fermentation on the cellulose hydrolysate. The two strains designated TVA1 and DRL99 showed better fermentation characteristics on the hydrolysates than did the other strains tested. Strains TVA1 and DRL99 were also able to acclimatize to higher hydrolysate concentrations at faster rates than were the other strains tested (Figure 16). The acclimatized strains derived from TVA1 and DRL99 were designated CASH1 and CASH2, respectively.

S. cerevisiae CASH1, which showed tolerance to both hemicellulose and cellulose hydrolysate, as well as the best acclimatization rate on cellulose hydrolysate, was selected as the process microorganism. Maintenance of the acclimatized (hydrolysate-tolerant) phenotype in strain CASH1 was shown to be dependent on maintaining the yeast in hydrolysate-containing media.

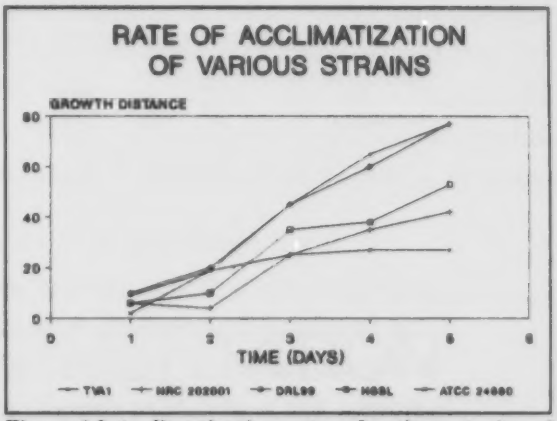


Figure 16. Acclimatization rates of various strains of *S. cerevisiae*

5.2 Hydrolysate Fermentability

A number of cellulose hydrolysis runs were carried out in the plug flow reactor using different reactor conditions to 1) determine the effect of reactor conditions on cellulose-to-glucose conversion, 2) measure the amounts of suspected inhibitory compounds (e.g. 5-hydroxymethyl furfural) generated using different reactor conditions, and 3) determine the fermentability of the resulting cellulose hydrolysate streams. Table 4 (Section 4.2.2.1) shows data for a number of these runs. Fermentability was considered to be good if a hydrolysate with a fermentable sugar concentration of over 6% fermented at 50% of the rate of a control (i.e., Effective hydrolysate Concentration, or $EC_{50} > 6\%$). Moderately fermentable hydrolysates showed effective hydrolysate concentrations of between 2 and 6%. An effective hydrolysate concentration of less than 2% was given a rating of poor fermentability.

It was found that, in those reactor runs where more than one of the three reactor variables (reaction time, reaction temperature, and acid concentration) were at high levels, the resulting hydrolysates were poorly fermentable. Runs in which only one of the variables was at the high level not only resulted in reasonable conversions of cellulose to glucose but also yielded fermentable substrates. In the cases where the conditions were mild for all three of the physical parameters, the product was very fermentable, but the conversion of cellulose to glucose was unacceptably low.

In order for the CASH process to be economically viable, conditions for the production of glucose from cellulose must be severe enough to give a reasonably high yield of glucose from cellulose (>40%), while at the same time mild enough to produce a fermentable product. Tests on the products listed in Table 4 and on the "optimal" hydrolysates listed in Table 5 suggest the existence of a threshold cellulose-to-degradation product conversion of approximately 15%. If the cellulose-to-degradation products conversion exceeded this value, the hydrolysates were typically not very fermentable. The conditions which appear to be best suited to remaining below this "threshold" are those of high temperature combined with low residence time and low acid concentration. Achievement of high cellulose-to-glucose conversions often meant exceeding this "threshold". The resultant hydrolysates contained high levels of inhibitors, and fermentation EC_{50} values were found to be low (i.e., the product was more toxic). It seems, therefore, that in order to ensure fermentability of the product, the reactor conditions

should be held slightly to the mild side of the cellulose-to-glucose conversion peak maximum.

5.3 Small-scale Batch Fermentations

After determination of the optimum reactor conditions for cellulose hydrolysis in the plug flow reactor, and of the EC_{50} values for the associated hydrolysates, small-scale batch fermentations were carried out with 50/50 mixtures of hemicellulose and cellulose hydrolysates. Hemicellulose hydrolysate was used at the concentrations expected from the first stage hydrolysis process (50 to 60 g/L fermentable sugars), and was CaO/sulphite treated. The cellulose hydrolysate used was from run 2U, at a concentration slightly below its determined EC_{50}. Figures 17 and 18 show time courses for a fermentation of mixed

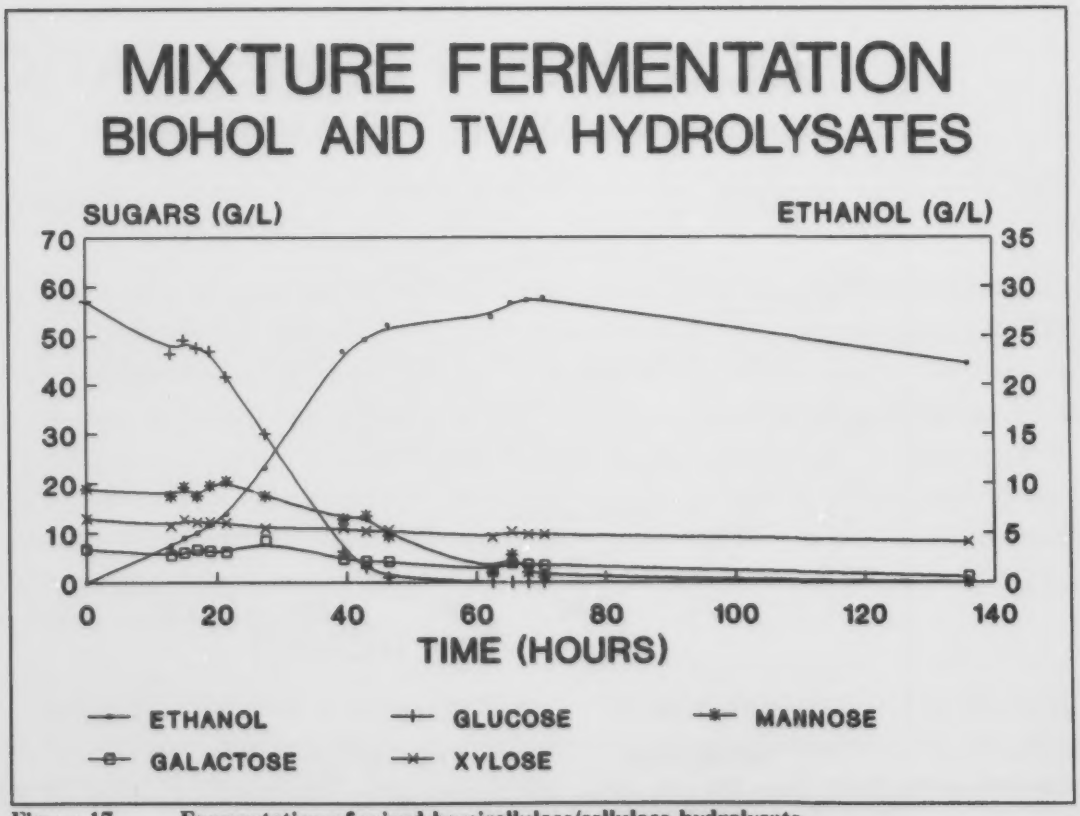


Figure 17. Fermentation of mixed hemicellulose/cellulose hydrolysate

hemicellulose and cellulose hydrolysates, and a control fermentation using a synthetic sugar mixture similar to that analyzed in the mixed hydrolysate, respectively. The latter (i.e.,control) was carried out in order to determine the kinetic parameters which could be attained in the absence of wood derived fermentation inhibitors. These fermentations used the acclimatized *S. cerevisiae* CASH1 strain. Glucose, mannose, galactose, xylose, arabinose, and ethanol were monitored throughout the fermentation. The xylose and arabinose did not appear to be utilized (the data for arabinose concentrations are not included in the figures). The ethanol concentration was found to decrease after the fermentable sugars were exhausted, due to evaporation of the ethanol in the exhaust gases of the fermenter. Evaporative losses of ethanol would have been occurring throughout the fermentation, but during the period of sugar utilization would be masked by ethanol production. Fermentations carried out later in the project used a condenser on the exhaust gases line to minimize this loss.

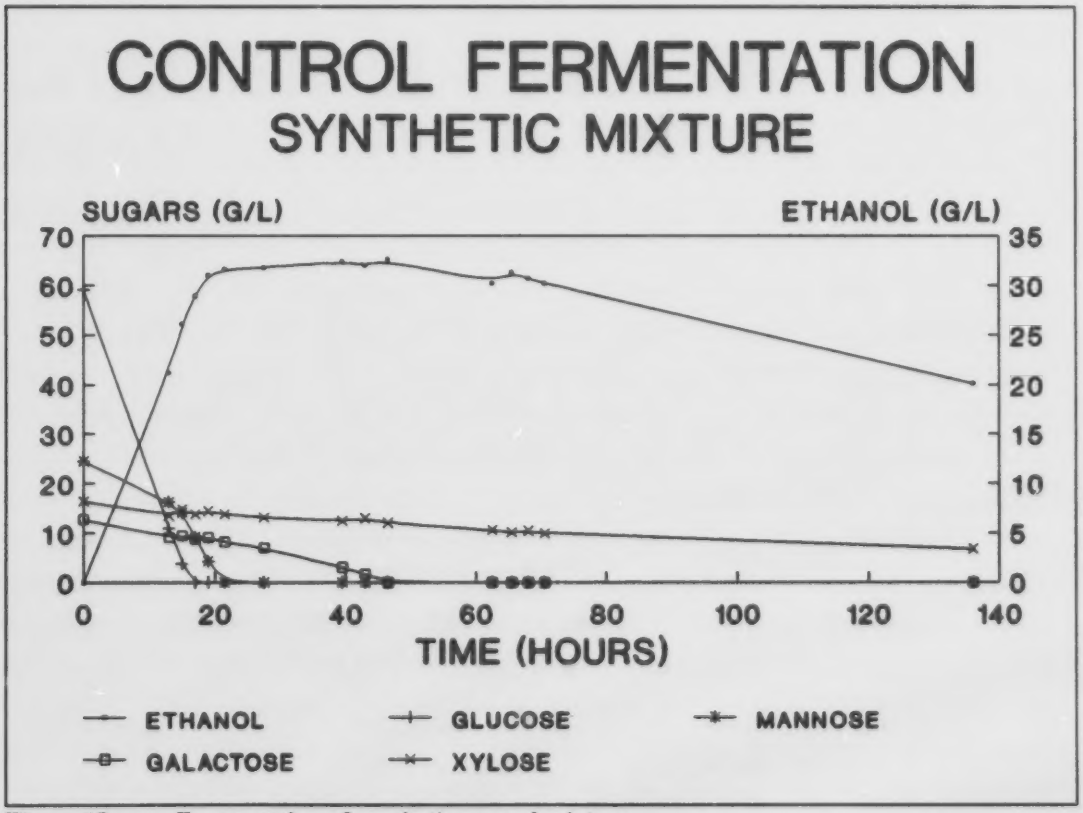


Figure 18. Fermentation of synthetic control mixture

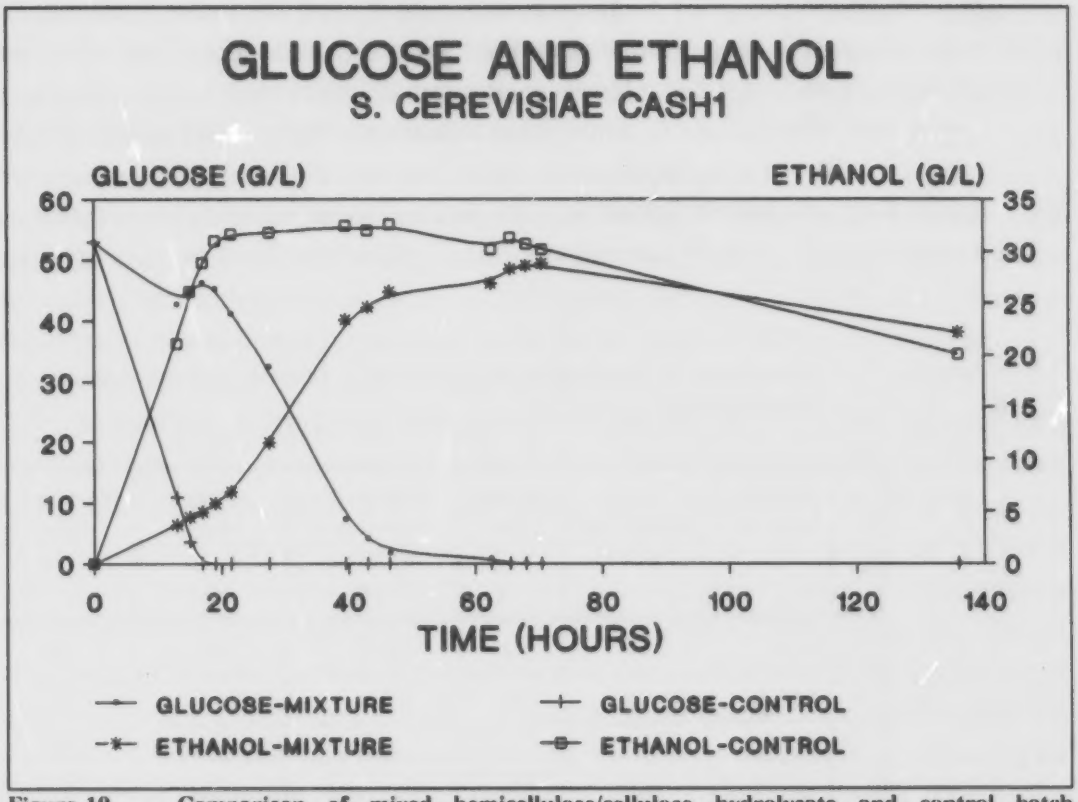


Figure 19. **Comparison of mixed hemicellulose/cellulose hydrolysate and control batch fermentations.**

The rates of sugar utilization and ethanol production were slower in fermentations of mixed hemicellulose and cellulose hydrolysates than in the control (see Figure 19). The mixed hemicellulose/cellulose hydrolysate fermentation had a slower growth rate than did the control. It is important to note that the final ethanol concentrations achieved in the two media were comparable, even though the mixture required a longer fermentation time than did the control. The ethanol yields found for both the mixture and the control were low--both of these fermentations had no condenser on the exhaust gases line, which would result in evaporative losses of ethanol throughout the fermentation. These evaporative losses are evident in the figures.

Several small-scale (1 litre) batch fermentations were carried out using mixed cellulose/hemicellulose hydrolysate as feedstock at various sugar concentrations, and using two different batches of cellulose hydrolysate. The two different cellulose hydrolysate

batches, produced during plug flow reactor runs 3G and 3H, showed different EC_{50} values, even though the reactor conditions used for their production were, on average, quite similar (see section 4.2.3). However, the sample which was tested from run 3G was a composite of the entire run, while the sample tested from run 3H was obtained late in the run when the reaction temperature had fallen and the reaction conditions were not as harsh. Synthetic control fermentations were also carried out at different fermentable sugar concentrations. Table 9 presents the kinetic parameters for a number of these runs.

Table 9. **Comparison of fermentation parameters with different cellulose hydrolysates at various concentrations.**

	CH batch used	Total fermentable sugar conc. (g/L)	Growth rate (hr^{-1})	Yield of product from substrate (g/g)	Final ethanol conc (g/L)	Ferment'n Time (hours)
1	SYN [a]	39	0.22	0.49	19.3	26
2	SYN [a]	72	0.23	0.44	31.4	50
3	3G	47	0.12	0.47	22.0	50
4	3G	69	0.05	0.47	31.9	70
5	3H	74	0.10	0.46	32.0	61

CH cellulose hydrolysate
a synthetic mixture of pure sugars

Two runs (1 and 2 in Table 9) were carried out using the synthetic (control) mixture of sugars at different starting sugar concentrations. It was found that, at fermentable sugar concentrations of 39 and 72 g/L, the exponential growth rate was comparable (0.22 and 0.23 hr^{-1}, respectively), and the sugar utilization rate, ethanol production rate, and yield of product from substrate were also comparable. The final ethanol concentration was, naturally, higher with the higher initial sugar concentration. The duration of the fermentations using synthetic media was shorter than in the mixture fermentations.

Two runs (3 and 4 in Table 9) were carried out using cellulose hydrolysate from plug flow reactor run 3G at two different initial fermentable sugar concentrations. The

fermentation media were prepared so that one-half of the total fermentable sugar was from cellulose hydrolysate, the other half from CaO/sulphite treated hemicelluiose hydrolysate. At the higher (69 g/L) sugar concentration, the exponential growth rate was lower (0.05 hr^{-1}) than for the lower sugar (47 g/L) concentration (0.12 hr^{-1}). After a slower growth phase, the rates of sugar utilization and ethanol production were comparable. Identical ethanol yields (92% of theoretical) were obtained at the different initial sugar concentrations. These observations may indicate that the inhibitory effects of the hydrolysates were manifested more during cell growth and did not significantly affect the production of ethanol from fermentable sugar or the sugar utilization by the yeast.

The hydrolyzate from plug flow reactor run 3H was found to have a higher EC_{50} (less toxic) than did that from run 3G. The last two rows of data in Table 9 shows that the cellulose hydrolysate from run 3H was indeed more fermentable than that from run 3G. At a slightly higher starting sugar concentration (i.e., 74 g/L vs. 69 g/L), the fermentation time for 3H was shorter, the growth rate was higher, while the final ethanol concentrations and yields were similar. This can be explained by the fact that, even though these two runs were carried out under similar plug flow reactor conditions (as similar as can be maintained in such runs), at the time of sampling for fermentation testing purposes, the actual conditions were milder in run 3H. This emphasizes the benefit of remaining on the mild side of the glucose production maximum when establishing reactor conditions.

5.4 Pilot-Scale Fermentations

Larger-scale fermentations were carried out on substrates containing a mixture (50/50) of cellulose (from run 3G) and hemicellulose (CaO/sulphite treated) hydrolysates, as in the small-scale batch fermentations. The acclimatized *S. cerevisiae* CASH1 strain was used. The glucose, mannose, galactose, xylose, arabinose, and ethanol concentrations were monitored throughout the fermentations (see Figures 20 and 21).

The rate of fermentation of the mixed hydrolysate at the pilot scale (100 litre working volume) was very similar to that at laboratory scale (1 litre working volume). It should be noted that during the first pilot-scale fermentation (shown in Figure 20), temperature control was lost due to mechanical problems during the run, and the

fermentation was conducted at a temperature of between 25 and 28°C, which may have resulted in some slight differences in the rate of fermentation, even though these appear to have been minor. Loss of ethanol due to evaporation is evident, as no condenser was used in the first pilot-scale run.

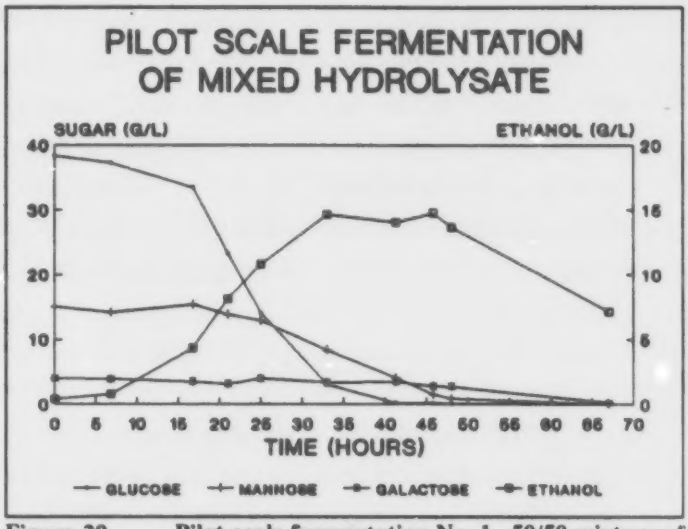


Figure 20. **Pilot-scale fermentation No. 1. 50/50 mixture of TVA/Bio-Hol hydrolysates**

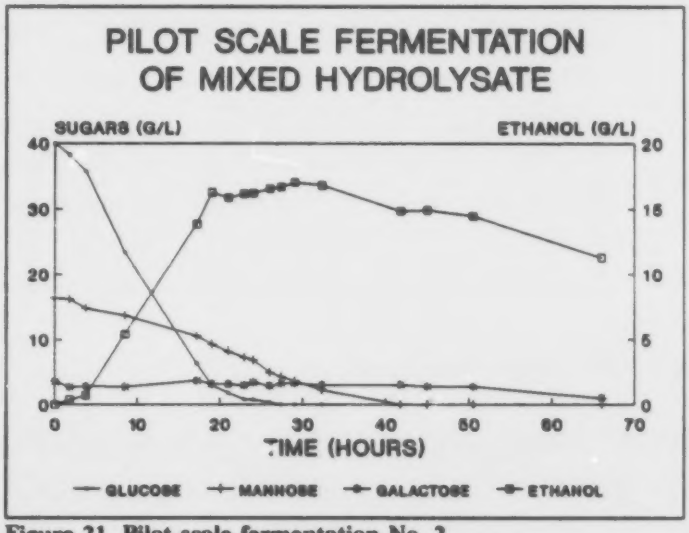


Figure 21. Pilot-scale fermentation No. 2

The second pilot-scale fermentation (see Figure 21) was carried out with proper temperature control. As well, a condenser was added to the exhaust gases line to minimize the evaporative loss of ethanol which was quite significant in the first run; this condenser was not completely effective, as some evaporative losses of ethanol are still evident. A larger (~10%) inoculum was used in order to allow better comparisons between the pilot-scale (100 litre) and small-scale (1 litre) fermentations. The second fermentation was complete within 34 hours, with all of the glucose being consumed within 24 hours. The sugar utilization and ethanol production rates, as well as the exponential growth rate, were comparable to those obtained in the small-scale batch fermentations. The yield of ethanol from fermentable sugar was 0.32 g/g (63% of theoretical). This low value was largely due to evaporative loss of ethanol throughout the duration of the fermentation, but could be partly due to the production of other compounds.

Both of the pilot-scale fermentations were carried out using initial fermentable sugar concentrations of approximately 50 g/L. This concentration was used because of the EC_{50} values which were determined for the cellulose hydrolysate produced in run 3G. Based on the smaller-scale fermentations at higher concentrations of hydrolysates (e.g., Run 5 in Table 9) and the fact that the fermentation parameters at the small scale and pilot scale were very similar when using the same conditions, pilot-scale fermentations could be carried out at sugar concentrations of up to 70 to 80 g/L (assuming all other parameters were the same). As well, the use of a hydrolysate produced under slightly milder conditions (such as run 3H) should result in fermentation kinetics at higher starting sugar concentrations comparable to those found at small scale (e.g., run 5 in Table 9).

5.5 Nutrient Requirements

The yeast extract used during both the small and large-scale fermentations is impractical for full-scale industrial fermentations because of its prohibitive cost. Therefore, inexpensive additives which could be used to replace the yeast extract were sought. Using a statistical analysis procedure known as the Plackett-Burmann technique (Stowe and Mayer, 1966) extensive work was carried out in order to determine the components of the yeast extract that were necessary for the fermentation to proceed at maximal rate. The trace elements and other additives found to be required by *S. cerevisiae* CASH1 are listed in Table 10. The exact concentrations of each nutrient required were not determined--the concentrations listed in the table are those present in Difco yeast extract, and are adequate for the growth of this yeast strain.

Table 10. Nutrient Requirements for *S. cerevisiae* CASH1

NUTRIENT	CONCENTRATION (mg/L)
Organic Nitrogen	400
Phosphate	690
Magnesium	50
Thiamine	0.25
Calcium Pantothenate	0.50
Riboflavin	0.175
Biotin	0.01

Since the requirements of the process are now known, additives may be combined to provide all of the essential nutrients. Once the location of the process plant is decided upon, local availability of the various nutrients can be determined. Another option might be to hydrolyze the spent yeast from the fermentation and use it as a nutrient source.

5.6 Effect of pH on EC_{50}

Adjusting the pH over the range of 5.5 to 8.5 was found to have a minimal effect on the fermentation of cellulose hydrolysate.

5.7 Effect of Berocell 439 on EC_{50}

A range of concentrations of Berocell 439, a flocculating agent used in the separation studies, was examined for possible inhibitory effects on the fermentation. Concentrations of Berocell 439 as high as ten times the concentration likely to be used showed no inhibitory effects.

5.8 Effect of Clean-up Procedures on EC_{50}

Several procedures for the removal of inhibitory compounds from the hydrolysates were studied. Procedures which were considered to be too costly to be used in the final process were examined in the hope that they would define the chemical nature of the inhibitors and provide some insight into possible less expensive methods for their removal.

Among the processes examined were ion-exchange, solvent extraction, and treatment with activated carbon. The ion-exchange and activated carbon treatments were not found to significantly affect the fermentability of the cellulose hydrolysate. The solvent extraction treatment was used in order to provide samples for Gas Chromatography/Mass Spectroscopy (GC/MS) analysis. This demonstrated that one of the major components extracted from the cellulose hydrolysate was 5-hydroxymethyl furfural, an expected inhibitor in the fermentation (Faber *et al.*, 1982).

A treatment described by Leonard and Hajny (1945), involving the use of CaO and sodium sulphite, was found to appreciably improve the fermentability of the hemicellulose hydrolysate. It is unknown at this time what inhibitors this treatment might be removing. A more detailed study of the CaO/sulphite treatment, combined with "flashing" of the volatiles in the TVA hydrolysate, is described in the next section.

5.9 Effect of Flashing of Hydrolysate on EC_{50}

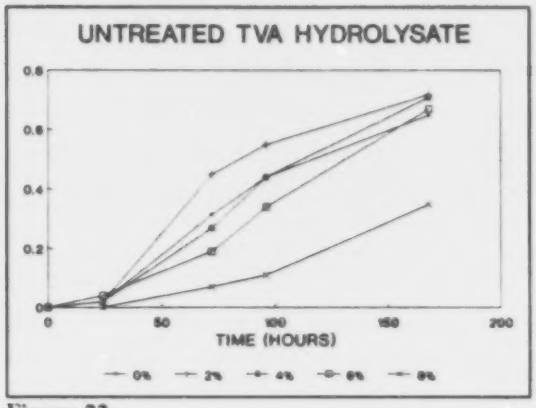


Figure 22

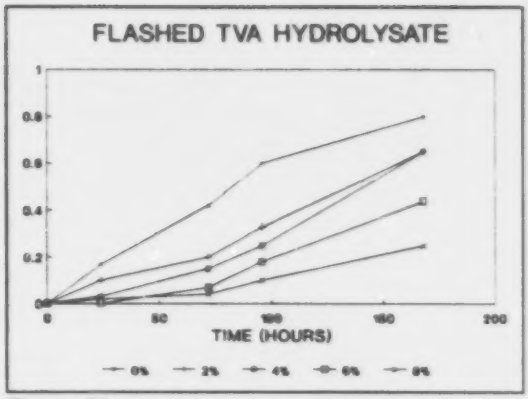


Figure 23

Hemicellulose hydrolysate, received from TVA, was flashed in the plug flow reactor (total residence time of 2.3 minutes) from a temperature of 160°C directly to atmosphere. It was intended that flashing to atmosphere in this manner would aid in the removal of some of the volatile inhibitors introduced during the hydrolysis process (i.e., SO_2, acetic acid, furfural). Furthermore, this would simulate what takes place after the first stage hydrolysis reactor in the full-scale process (i.e., stepwise flashing in which a significant portion of these relatively volatile constituents would end up in the vapour phase). While EC_{50} determinations were being carried out on this material, further examination of the CaO/sulphite treatment, on both the flashed and unflashed material, was also performed.

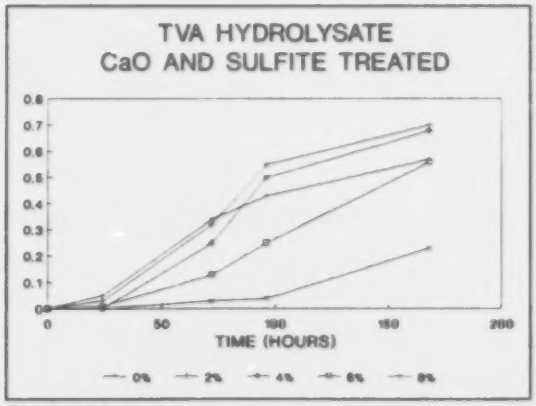


Figure 24

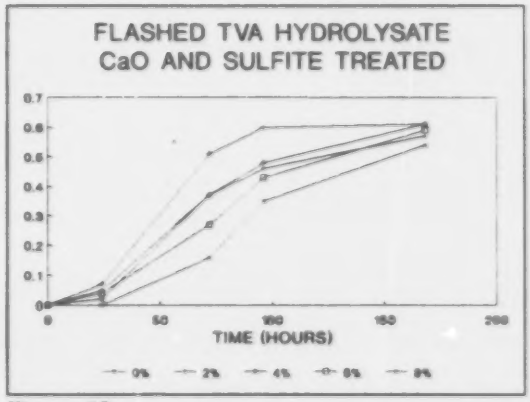


Figure 25

The results, shown in Figures 22 through 25 (which are graphs of weight loss due to CO_2 evolution versus time), showed that the flashing process did not result in a more fermentable product, but that CaO/sulphite treatment of the flashed material had a positive effect. This treatment resulted in reasonable fermentation rates with as high as 8% hydrolysate (all other treatments showed inhibition at the 8% level).

5.10 Effect of Salts on Fermentation Activity

High salt concentrations were found to decrease the relative growth rate, rate of ethanol production, rate of sugar consumption, and the final ethanol concentration during fermentation. In general, sulphates were tolerated better than acetates and chlorides, and magnesium salts were less inhibitory than ammonium, calcium, and sodium salts. It should be noted that the salt concentrations which proved inhibitory were significantly higher than those expected as a consequence of neutralizing the hydrolysates.

6. SEPARATION RESULTS

Separation of the liquid (i.e., sugar) stream from the residual cellulose/lignin of the second stage hydrolysis product is an important process section of the prospective plant. Due to the fineness of the suspended solids, clarifying the sugar stream while maximizing the dryness of the residual solid was not an easy task. A number of equipment modifications were made to the decanter feed system which allowed for: heating of the feed, maintaining a well-dispersed feed, and delivery of feed to the decanter at variable but uniform flow rates.

Liquid/solid separation of the products of second stage hydrolysis took place throughout the entire course of the project prior to fermentation evaluation. Though good separations were consistently achieved, a more systematic study of the operating parameters was necessary. This study was specific to our equipment in terms of separation efficiencies, flow rates, etc., but would reveal general trends which could be expected with larger-scale equipment.

The operating parameters studied were feed solid content, feed flow rate, feed temperature and the presence or absence of the flocculant Berocell 439. The results of the 16 experiments conducted are shown in Table 11. This table was organized to be readily amenable to statistical analysis. The complete table of results appears in Appendix D (Table D.1).

Table 11. Results of Factorial Separation Experiments

Expt. No. (see App. D)	Treatment Combination*	Susp. Sol. FEED (%)	Susp. Sol. OVERS (%)	Susp. Sol. UNDERS (%)	% SUGAR Recovery (**)	% SUSP. SOL. Recovery (***)
SEP-L	(1)	5.5	1.6	22.6	85.0	76.1
SEP-B	a	11.4	3.2	26.0	69.9	81.7
SEP-K	b	5.5	2.1	24.0	85.0	76.1
SEP-A	ab	11.4	6.2	28.4	80.7	58.5
SEP-N	c	5.5	0.0	22.5	80.4	99.8
SEP-D	ac	11.4	2.2	26.3	68.0	87.9
SEP-M	bc	5.5	1.6	23.4	85.8	76.0
SEP-C	abc	11.4	5.1	28.8	78.0	67.1
SEP-Q	d	7.6	1.2	23.0	83.8	61.2
SEP-G	ad	9.5	2.3	21.8	68.0	84.7
SEP-P	bd	7.6	3.7	23.9	83.8	61.2
SEP-F	abd	9.5	5.7	22.0	79.9	53.8
SEP-S	cd	7.6	0.0	27.0	77.1	99.9
SEP-I	acd	9.5	1.6	23.6	69.8	89.5
SEP-R	bcd	7.6	2.6	26.5	83.2	72.6
SEP-H	abcd	9.5	5.1	22.7	78.9	59.6

* When letter appears, the variable it represents is at the high level. (1) represents the experiment in which all of the variables are at their respective low levels.

- a feed Dry Solids (total); Hi: 14-15% DS, Lo: 8-10% DS
- b feed Flow rate Setting; Hi: 60% full scale, Lo: 40% full scale
- c feed Temperature; Hi: 65-75°C, Lo: 15-25°C
- d Berocell; Hi: 0.02% based on DS, Lo: none.

** % Sugar Recovery in OVERS = (Sugar Flow in OVERS)/(Sugar Flow in FEED)*100%

*** % Susp. Sol. Recovery in UNDERS = (S. Sol. Flow in UNDERS)/(S. Sol. in FEED)*100%

6.1 Effect of Separation Parameters on Sugar Recovery

The data were analyzed using a factorial method, and several significant relationships were observed. The statistical tables themselves are included in Appendix D (Tables D.2 and D.3).

The "% sugar recovery" is equal to the ratio of sugar flow in the overs to sugar flow in the feed stream. Both the feed solid content and feed flow rate were found to have a significant effect on the sugar recovery at a 1% level of significance. The sugar recovery dropped with increasing feed solids. When high feed solids are present, both the density and the viscosity of the liquid phase are increased. The relative density of the solid to the liquid phase is decreased and so, consequently, is the driving force for separation. The viscosity of the liquid phase relates to the drag force that the particles encounter in falling out of suspension. Therefore, in the case of higher feed solids, there is more resistance to sedimentation, the particles have a lower terminal velocity, and don't settle as quickly. There could also be more interactive effects whereby the particles interfere with each other.

The sugar recovery increased with increasing feed flow rate. At higher feed flow rates, the proportion of overs flow to feed flow was increased. Even though the level of suspended solids in the overhead stream was also increased, proportionally more water was flowing in the overs at high feed rates than at low feed rates, thus accounting for the improved sugar recoveries. Although the solid content of the underflow stream was higher at the higher solid loadings (i.e., higher feed flows), much more of the suspended solid was lost in the overs stream than at low feed flows. Nevertheless, in terms of sugar recovery, this higher suspended solid content of the overs stream was more than compensated for by the greater water flow rates. This trend may be specific to the design of the decanter or the relative lengths of the clarifying and drying zones, which is controlled, in our equipment, by a "regulating ring". Presently, there is a large diameter ring (short clarifying, long drying) in place, implying that there is less resistance to the flow of the liquid stream and therefore a shorter liquid residence time and less clarifying.

Berocell had a significant detrimental effect on the sugar recovery at a 1% level of significance, although this effect appears to be mainly due to an interaction with the feed solids content. At high feed solids, Berocell had no effect on sugar recovery while at low

feed solids the presence of Berocell decreased the sugar recovery. At high feed solids the viscosity of the liquid phase was high, regardless of the presence or absence of Berocell, while at low feed solids Berocell significantly increased the viscosity and this effect seemed to counteract its flocculant properties.

Feed temperature did not significantly affect the sugar recovery even though it did improve the separation efficiency (i.e., clarifying of overs stream or recovery of suspended solids). This implied that sugar recovery was more flow dependent while the solids recovery was separation dependent.

The feed solids-flow interaction was significant at a 1% level of significance. Feed flow rate had a more significant effect on sugar recovery at high feed solids because flow rate had a greater effect on solid loading at the higher feed solid concentration.

The feed temperature-Berocell interaction was significant at a 5% level. Berocell had a greater effect at low temperature (i.e., Berocell resulted in a larger drop in sugar recovery) because of the viscosity consideration. This was especially true at low feed solids.

6.2 Effect of Separation Parameters on Recovery of Suspended Solids

Suspended solids recovery refers to the percentage of the undissolved solids in the feed that are recovered in the underflow or sludge stream. From the statistical analysis it was evident that feed solids, flow and temperature all had a significant effect (1% level) on the recovery of suspended solids.

As feed solids were increased the recovery of suspended solids decreased. The accompanying increase in the viscosity and density of the aqueous phase decreased the Stokes terminal velocity of the particles, and hence, made it more difficult to remove the material from suspension.

An increase in the feed flow rate had an adverse effect on suspended solids recovery. A higher feed flow rate meant a lower residence time and without a simultaneous increase in the terminal velocity of the particles, the solid recovery decreased.

A higher feed temperature improved the recovery of suspended solids. The higher temperature decreased the viscosity of the liquid phase and resulted in an increase in the density difference between the solid and liquid phases. Thus, the particle terminal velocity was increased and the separation efficiency was improved.

Berocell proved to be insignificant in terms of its effect on recovery of suspended solids. However, the Berocell-flow interaction was significant at a 5% level. At high flow rates Berocell decreased the solid recovery. Again, this was likely a viscosity and residence time effect. At low flow rates Berocell had no effect because the increased residence time likely compensated for the higher viscosity.

6.3 Summary of Trends and Choice of Operating Conditions

It must be re-emphasized that the purpose of this separation analysis was to indicate trends and that the actual numbers achieved are specific to the equipment used.

Increasing the feed solids resulted in a lowering of both the sugar and suspended solids recoveries. In the interests of facilitating separation, a dilute feed would therefore be used. However, the economic implications of fermenting the resultant dilute sugar solutions must be compared to having a more concentrated feed but losing some sugar in the underflow. A concentrated feed would negate the need for evaporation of the sugar stream but may create other downstream processing problems such as the fouling of fermenters and distillation columns with suspended solids. Note that the mass balance model foresees a total feed solids content of 14% to the first decanter in the three stage counter-current washing system.

Feed flow rate was the one variable where conflicting effects were observed. Higher feed rates improved the sugar recovery (note, this might be equipment specific) while at the same time they decreased the suspended solids recovery. Hence, feed rate must be optimized in order to maximize both of these measures of separation efficiency, or it may be decided to accommodate the more important of the two based on an economic analysis.

Increasing the temperature of the feed had no effect on the sugar recovery but markedly improved the recovery of suspended solids. Sugar recovery was more flow

dependent, while suspended solids recovery was more indicative of the degree of separation which occurred. A feed temperature of 70-85°C is expected in the plant. This would be classified as a "high" feed temperature, and would improve the separation while not affecting the sugar recovery.

Berocell had no positive effects on the separation and, assuming that it is representative of homopolymeric flocculants, it would be concluded that there is no merit to adding this type of flocculant to the feed suspension. Nevertheless, one should not rule out the possibility that another type of flocculating agent may improve the separation characteristics of this liquid/solid stream.

7. THE CASH PROCESS BLOCK DIAGRAM

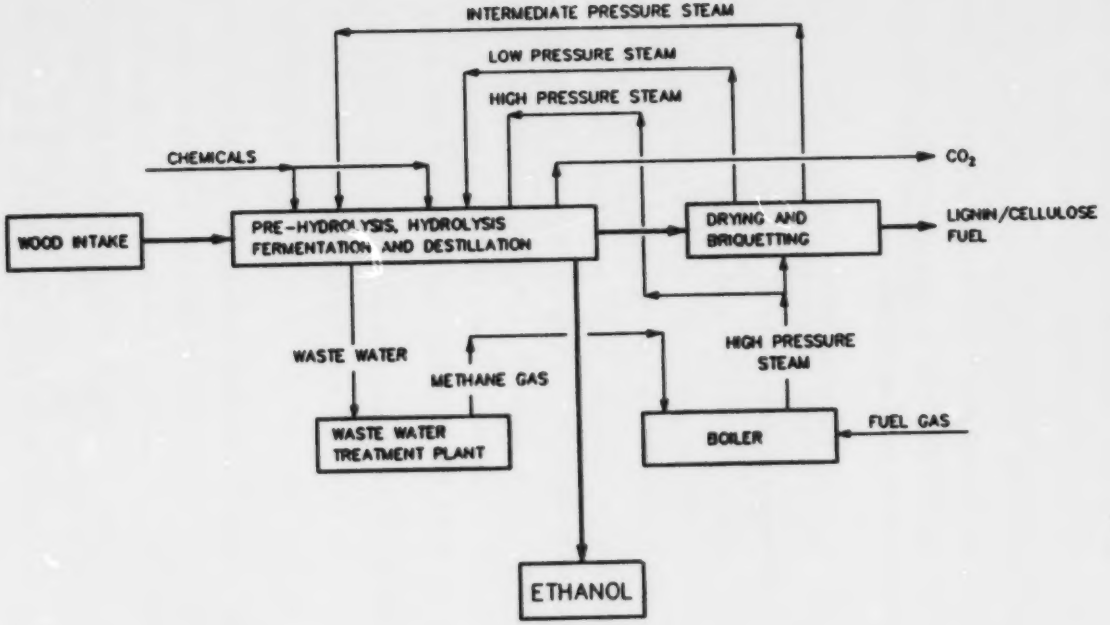
Block diagram 1-351-00 is an overview of the CASH process. The process produces both ethanol and a lignin/cellulose fuel. The process design is modular such that the process areas can be easily and independently modified. Because of this modular design, it is possible to incorporate new technologies that are developed subsequent to the commissioning of the CASH plant. The equipment in all process blocks is obtainable with both process and mechanical guarantees.

7.1 Wood Intake

The raw material for the CASH process can be one of a number of lignocellulosics. The main criterion is that the potential yield of hexose sugars is at least 30% of the dry weight of the feed material. Any l ignocellulosic is technically possible as a feedstock, but not all are economically feasible. Cost and process ethanol yield dictate the suitability of the raw material.

Among the most desirable raw materials is sawdust from conifers since there is an abundance of this material and it is a nuisance in many locations. Being a largely unused waste material, it is relatively low in price. Conifers are preferable because the concentration of hexose precursor is high and hexoses are the only sugars that have been commercially fermented.

Availability and cost of raw materials varies considerably according to location. The CASH process is designed to accept many lignocellulosic raw materials, generally with minimal modification. Raw materials could include various wood species, agricultural waste, and other lignocellulosic wastes such as paper.



CASH PROCESS
BLOCK DIAGRAM
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7.2 Prehydrolysis, Hydrolysis, Fermentation, and Distillation

7.2.1 Prehydrolysis

The equipment design for prehydrolysis is a modification of a modern continuous digester design used for producing pulp from various feedstocks. This basic pulp digester design has been used successfully with a variety of feedstocks including wood chips, sawdust, and agricultural waste such as bagasse.

The continuous prehydrolyzer offers many advantages over traditional batch hydrolyzers. These advantages include lower capital cost, shorter residence time (i.e., less down time), more amenable to automation and control, lower labour cost, and improved heat economy. Another significant advantage relates to the utilization of SO_2 as a catalyst. This permits the use of 316 stainless steel as the material of construction as opposed to the much more expensive reactor materials which have been used in previous prehydrolysis processes. Some of these more expensive reactor materials have included titanium, monel, zirconium and refractory linings. Thus, the use of SO_2 significantly lowers the capital cost of the plant. In addition, because a significant portion of the SO_2 can be recycled back to the process (as high as 80%), the chemical cost is lowered and waste water treatment is facilitated.

7.2.2 Hydrolysis

The equipment design for the hydrolysis section is one that has been used in many applications involving small particle-size feedstocks. The focal point of this design is the St. Lawrence Reactors plug flow reactor (SLR reactor). This plug flow reactor consists of a series of tube and shell heat exchangers with a patented pressure control device at the end of the series. The SLR reactor has been used commercially in modifying starches to produce paper sizings, adhesives, and sugars. In addition, there has been extensive pilot-scale experimentation with the SLR reactor in converting both agricultural residues and wood wastes to sugar for subsequent ethanol production.

The SLR reactor utilizes a two-phase liquid/solid system. The solid feed is slurried in water and pumped through the heat exchangers. The liquid state is maintained throughout the reaction (i.e., reactor pressure maintained above that of saturated water

at reaction temperature). This offers advantages mainly in reduced heat transfer area requirements and in equipment simplicity. This design permits quickly achievable high temperatures and thus very short residence times. The short residence times provide for reduced equipment costs. The requirement for a small particle-size feedstock is satisfied by the upstream prehydrolysis equipment.

7.2.3 Choice of Solid/Liquid Separators

Because of the nature of the materials involved, the requirements for liquid/solid separation after prehydrolysis are different from those after hydrolysis. The solid residue after prehydrolysis is very similar to paper pulp since only the hemicellulose has been removed. Conversely, the insoluble material after hydrolysis consists only of lignin and unreacted cellulose. This mixture is very fine and, as a result, the hydrolysis solids are much more difficult to dewater than are the prehydrolysis solids.

The liquid/solid separation device chosen for the prehydrolysis stage is a roller press. Roller presses have proven to be very effective in dewatering pulp, producing cakes which contain over 40% solids.

A very high driving force is required to separate the residual solid from the liquid product of the cellulose hydrolysis step. In order to clarify the liquid and achieve the necessary solids content in the cake, a scroll centrifuge was chosen.

7.2.4 Fermentation

Because only hexose sugars have been commercially fermented to ethanol, the design of the fermentation section was based upon yeast fermentation. Pentose fermentation technology may be incorporated when it becomes commercially available.

The fermentation process was designed as a continuous cascade system. Such layouts have been used in ethanol plants fed with grain as well as in wood-to-ethanol plants such as those based on the Scholler process. Thus, the layout of the fermentation vessels may be considered established technology. The problem was to find and/or develop

a process organism which was resistant to the known toxic effects of wood hydrolysates. This became one of the significant contributions of the CASH process.

A number of strains of *Saccharomyces cerevisiae* were tested based on their ability to grow on both the hemicellulose and cellulose hydrolysates. The most resistant of these strains were then acclimatized to the wood hydrolysates. The most tolerant strain which also showed the highest rate of acclimatization became the process organism known as *Saccharomyces cerevisiae* CASH1.

7.2.5 Distillation

The distillation process is much the same as those which exist in a great number of ethanol plants. The process is designed to produce azeotropic ethanol (95%) for use as a fuel, fuel additive, or chemical feedstock. If necessary the product may be dehydrated to produce 100% ethanol with the addition of either an extractive-distillation or a membrane-separation process module.

7.3 Wastewater Treatment Plant

The wastewater from distillation and secondary-steam condensate contains various organic pollutants. This wastewater is sent to the treatment plant where these contaminants are removed, in compliance with environmental legislation, and methane is generated and collected as a fuel.

7.4 Boiler

The boiler is a conventional boiler that generates high pressure steam to be used in the cellulose hydrolysis section and in drying the unreacted lignin/cellulose. The methane from the wastewater treatment plant contributes to the fuel requirements but is not sufficient to power the boiler without being supplemented with additional fuel. Fuel gas is shown as the outside fuel source on the block diagram.

7.5 Drying and Briquetting

The unreacted lignin/cellulose is dried with high pressure steam supplied from the boiler. The pressure of steam drops as the drying occurs and the resultant lower pressure steam is used for prehydrolysis and hydrolysis. The dried lignin/cellulose has a higher heating value than the incoming wood feed because of its lower water content and the fact that it is richer in carbon and hydrogen than the original wood. This material can be sold as a high value fuel.

8. PROCESS FLOW DIAGRAM AND DESCRIPTION OF PROCESS AREAS

The following descriptions and explanations refer to the process flow diagrams (PFD's) for the various process areas of the CASH ethanol plant. The PFD's are discussed in order of their appearance in the overall process and are included for easy reference.

8.1 Chip Unloading/Storage Area

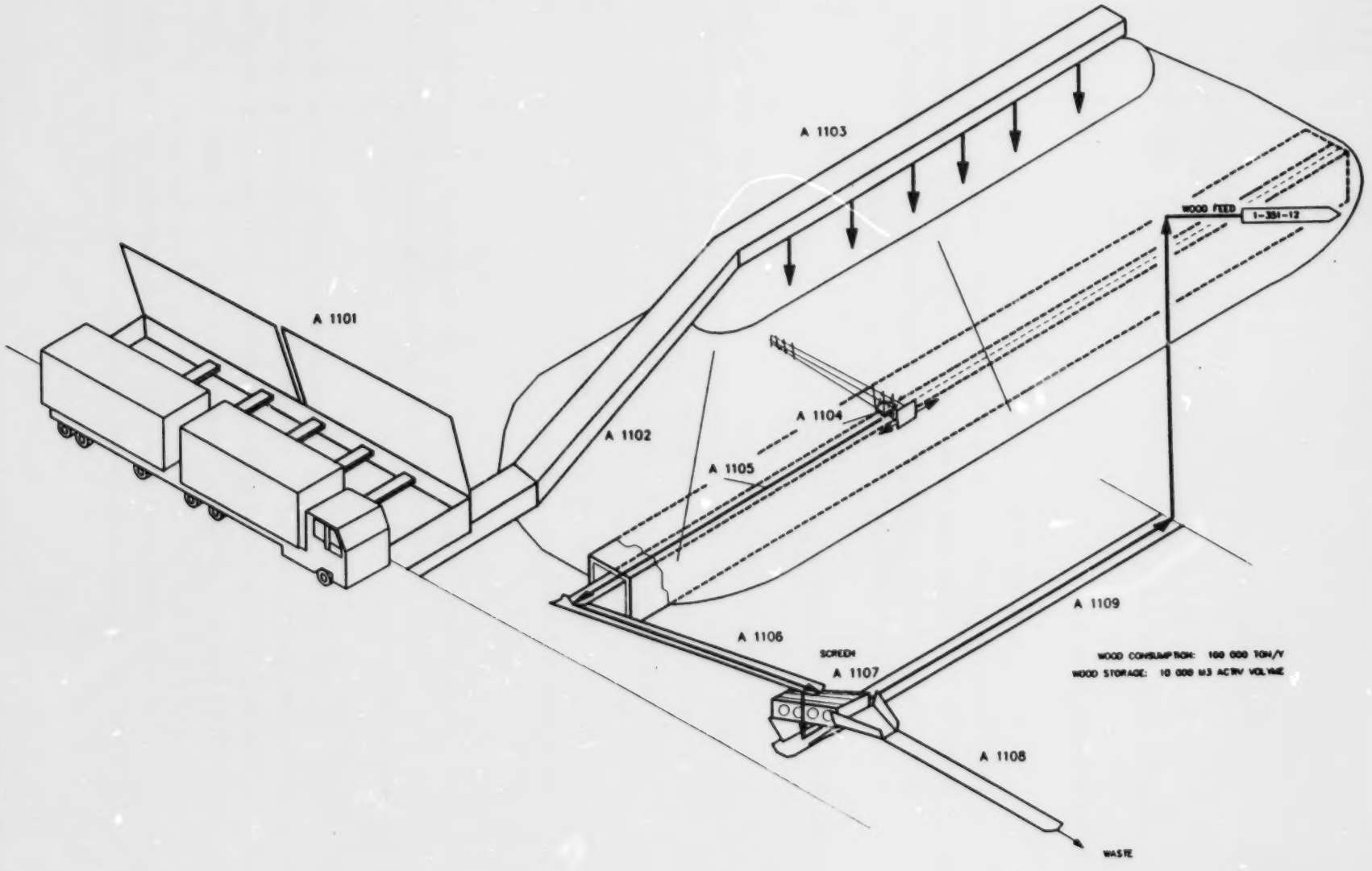
The feedstock procurement and storage area is depicted in PFD 1-351-01.

8.1.1 Truck Unloading Bin

Bin A-1101 is the entry bin for wood feed to the factory. All feed material is transported to the factory by trucks. These trucks are unloaded into receiving/storage bin A-1101.

8.1.2 Feed Transfer to Storage

The feed is conveyed both upward and horizontally from feed bin A-101 by belt conveyor A-1103. Once the feed is elevated and horizontal, it is distributed onto the concrete feed pad A-1102 through ports on conveyor A-1103, which can be opened as needed for even distribution of the feed onto pad A-1102. After falling onto the concrete storage pad A-1102, the wood feed is transferred, by a series of three conveyors, to screen A-1107. The first conveyor is a mobile conveyor, A-1104, which is self-loading and travels the entire area of the feed storage pad A-1102. This self-loading, travelling conveyor operates perpendicularly to stationary conveyor A-1105, which spans the entire length of storage pad A-1102 on one side. Conveyor A-1105 discharges onto conveyor A-1106, which is the final feed conveyor to the screen A-1107. The purpose of screen A-1107 is to remove oversized material from the wood feed prior to it being transferred downstream for processing. Screen A-1107 discharges the oversized material onto conveyor A-1108, where it is conveyed away as waste. This waste material is transported to a waste fuel boiler.



	WOOD HYDROLYSIS FEED STORAGE PROCESS FLOW DIAGRAM	
	SEDF	1-351-11-1-0

8.2 First Stage (Step 1) Hydrolysis

The prehydrolysis section, where the hemicellulose portion of the wood is hydrolyzed, is shown in PFD 1-351-13.

8.2.1 Steaming Vessel

Feed bin A-1301 serves as a feed accumulation vessel before the wood hydrolysis reactor and as a feedstock preheating vessel. Sawdust enters the feed bin A-1301, and is heated by waste steam from the process. This treatment helps expel air from the wood feedstock and renders it more amenable to impregnation with cooking liquor. Thus, a process function is served while at the same time conserving process energy.

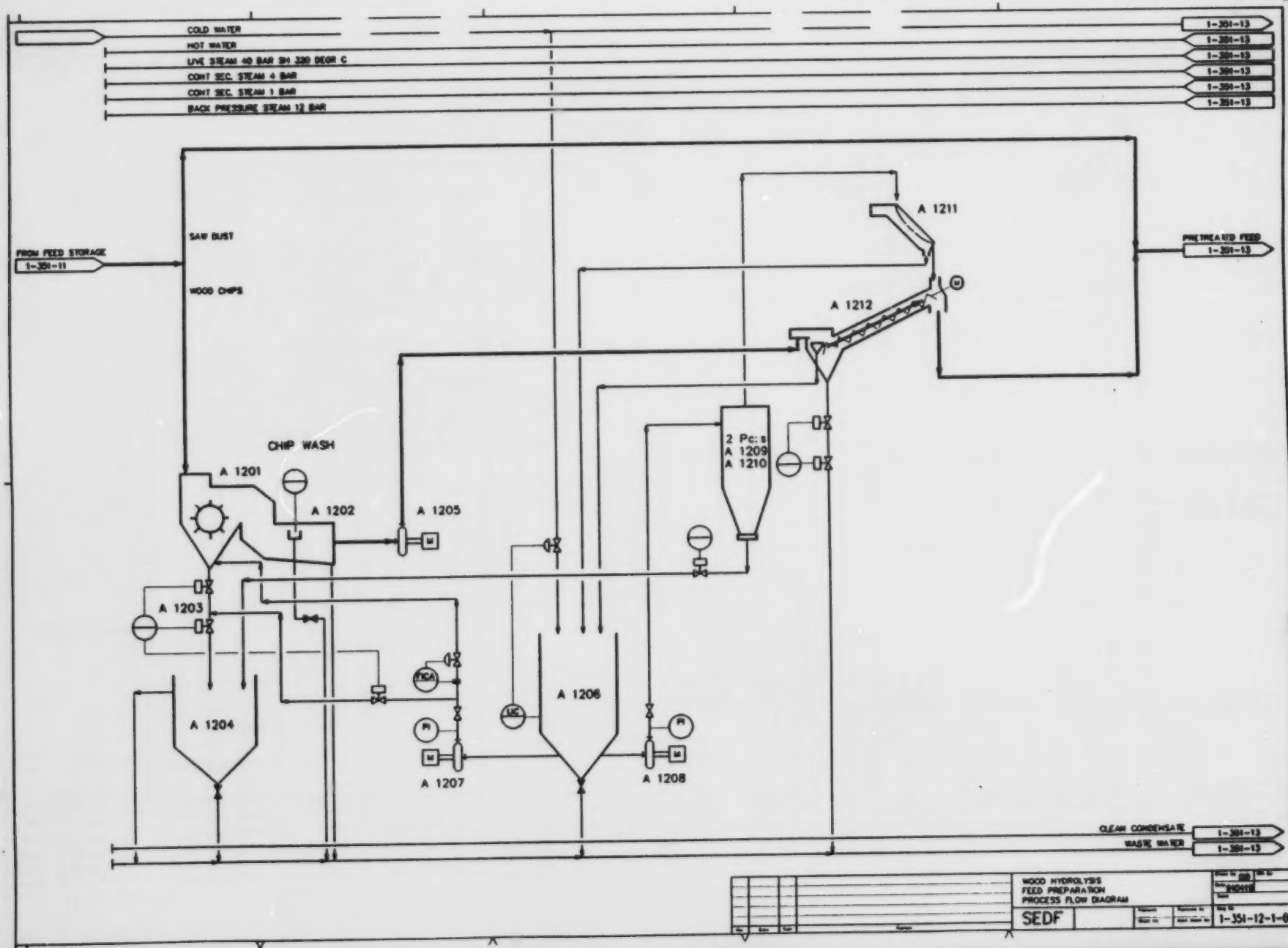
8.2.2 Step 1 Hydrolysis Reactor

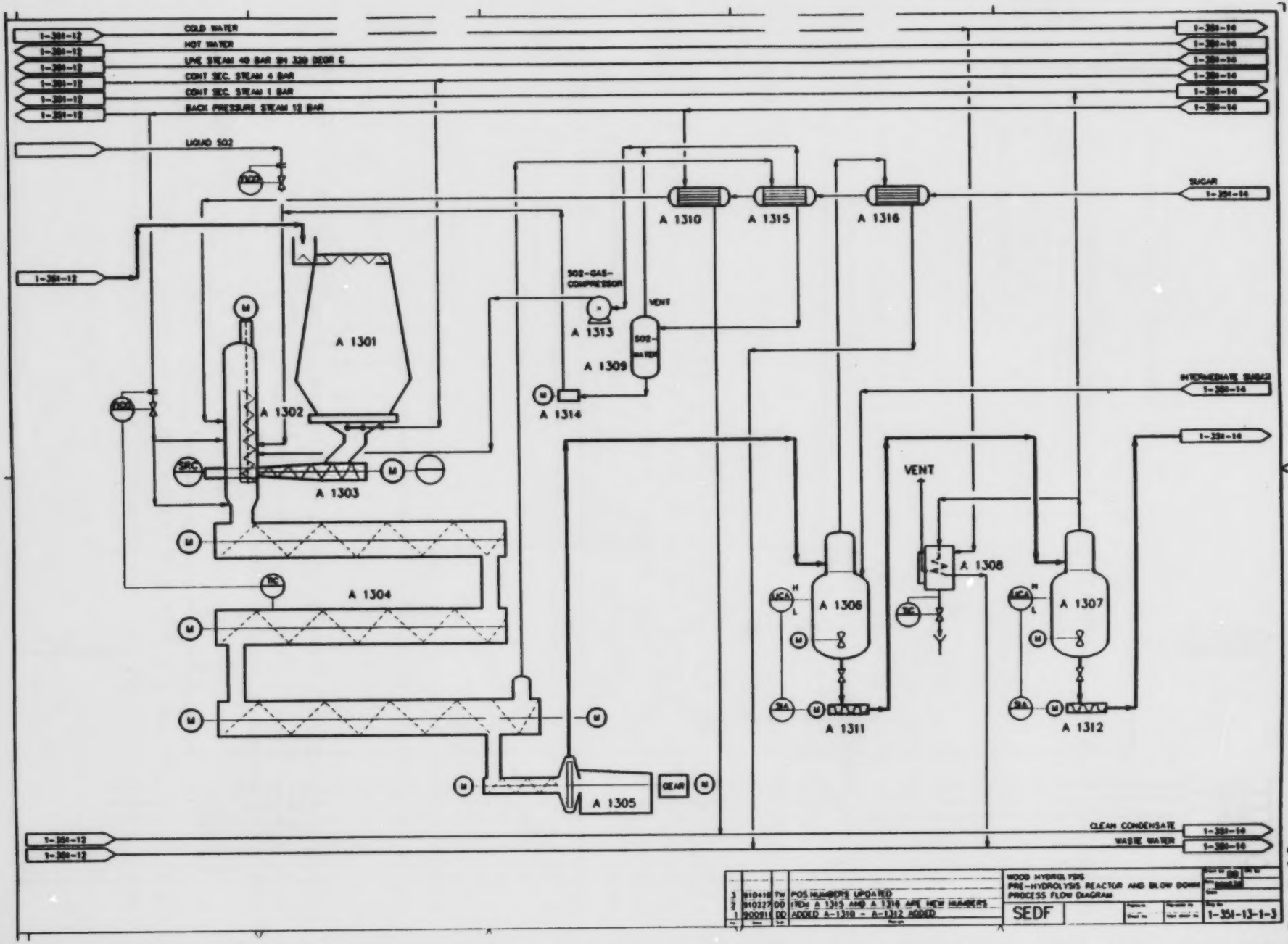
The particular equipment depicted in PFD 1-351-13 is designed for sawdust as a feedstock, though wood chips and other wood wastes can be accommodated. If wood chips are fed, it is necessary to install a chip-cleaning system upstream of the wood hydrolysis equipment (see PFD 1-351-12). From feed bin A-1301, the wood passes to the compression screw feeder, A-1303, which serves as a transition lock between the lower pressure in the feed bin and the higher pressure in the reactor. This is accomplished by compressing the wood into a plug and forcing it into the impregnation vessel system, A-1302.

In the impregnation system, there is a conveying screw system, A-1302, that mixes the wood with SO_2. As the wood leaves the conveying screws, it is mixed with recycled sugar solution.

The hemicellulose polymer in the wood is hydrolyzed in the reactor, A-1304. This results in the solubilization of the hemicellulose, while cellulose and lignin remain in the solid phase. This hydrolysis of the hemicellulose produces sugars along with other substances, such as acetic acid, whose precursors exist in the hemicellulose polymer.

From the reactor, the reaction mixture flows through a disk mill, A-1305, which further reduces the particle size of the remaining solid residue (especially knots and other


COLD WATER
HOT WATER
LIVE STEAM 40 BAR SH 320 DEGR C
CONT SEC. STEAM 4 BAR
CONT SEC. STEAM 1 BAR
BACK PRESSURE STEAM 12 BAR
1-351-13
FROM FEED STORAGE
1-351-11
SAW DUST
WOOD CHIPS
A 1211
A 1212
PRETREATED FEED
CHIP WASH
A 1201
A 1202
A 1205
2 Pcs
A 1209
A 1210
A 1203
A 1204
A 1206
A 1207
A 1208
CLEAN CONDENSATE
WASTE WATER
WOOD HYDROLYSIS
FEED PREPARATION
PROCESS FLOW DIAGRAM
SEDF
1-351-12-1-0


COLD WATER
HOT WATER
LPS STEAM 40 BAR SH 330 DEGR C
CONT SEC. STEAM 4 BAR
CONT SEC. STEAM 1 BAR
BACK PRESSURE STEAM 12 BAR
LIQUID SO2
SUGAR
A 1310
A 1315
A 1316
SO2-GAS-COMPRESSOR
VENT
A 1313
A 1309
A 1314
A 1301
A 1302
A 1303
A 1304
A 1305
GEAR
VENT
A 1308
A 1306
A 1307
A 1311
A 1312
CLEAN CONDENSATE
WASTE WATER
3 910418 TW POS NUMBERS UPDATED
2 910227 DD VIEW A 1315 AND A 1316 ARE NEW NUMBERS
1 900911 DD ADDED A-1310 - A-1312 ADDED
WOOD HYDROLYSIS
PRE-HYDROLYSIS REACTOR AND BLOW DOWN
PROCESS FLOW DIAGRAM
SEDF
1-351-13-1-3

large pieces of unreacted wood), making it easier to process in later steps. The disk mill, A-1305, is probably not necessary for processing sawdust. It is included in the design for wood chip processing.

8.2.3 Blow Down

The reaction mixture of solid and liquid flows to a series of two blow tanks, A-1306 and A-1307, which reduce the pressure of the reaction product mass (and allow recovery of secondary steam), so that the solid and liquid phases from the reaction can be separated and further processed. There are two blow tanks because this allows the recovery of some higher grade (4 bar) steam which can be used elsewhere. The positive displacement pumps, A-1311 and A-1312, are designed especially for pumping the high-density slurry which exits the blow tanks.

8.2.4 Steam and Heating System

The condenser, A-1308, condenses the flash steam from the final blow tank, A-1307. Because this flash steam contains some volatiles such as furfural and acetic acid, the condensate from this condenser is sent to the wastewater treatment plant.

There are three heat exchangers in series (A-1310, A-1315, and A-1316), which serve to preheat the sugar solution, which is recycled from the next step, prehydrolysis wash and separation. This sugar stream is recycled in order that the concentration of the hemicellulose sugar product is maximized. Such a step is possible in the prehydrolysis section because very little sugar degradation takes place under the reaction conditions employed. The only fresh water which enters the reactor is from the feedstock itself and from the 12 bar steam that is used to pressurize the reactor and help transport the reaction mass through the reactor. For economic reasons, the use of the 12 bar steam is minimized.

Considering the heat sources for the individual heat exchangers, the flash steam from the first blow tank, A-1306, supplies heat for A-1316. The condensate from this steam contains furfural and acetic acid and is sent to the wastewater treatment plant, along with the steam condensed from the second blow tank.

Heat exchanger A-1315 is part of both the SO_2 recycle system, and the recycle-sugar preheating system. The heat source for A-1315 is steam withdrawn from the end of the reactor, A-1304. Enough steam is withdrawn to supply 80 per cent of the SO_2 requirement for the reactor. The SO_2 contained in this steam is, for the most, part non-condensable. Most of the SO_2 entering heat exchanger A-1315 travels as a gas to the gas compressor, A-1313; this SO_2 is then injected into the wood feedstock entering the impregnation vessel, A-1302. The steam that travels with the SO_2 is condensed as it preheats the sugar solution. As this steam is condensed, it is collected in accumulation tank, A-1309. This condensed steam, and the small amount of SO_2 that it contains, is combined with the liquid makeup that is added to the wood feedstock in impregnation vessel, A-1302, by means of the pump, A-1314. The final heat exchanger, A-1310, is heated from the same 12 bar steam source as is used to pressurize the impregnation vessel and the reactor. The condensate from heat exchanger A-1310 is clean, so it is returned to the steam plant for reuse.

8.3 Step 1 Prehydrolysis Washing and Separation

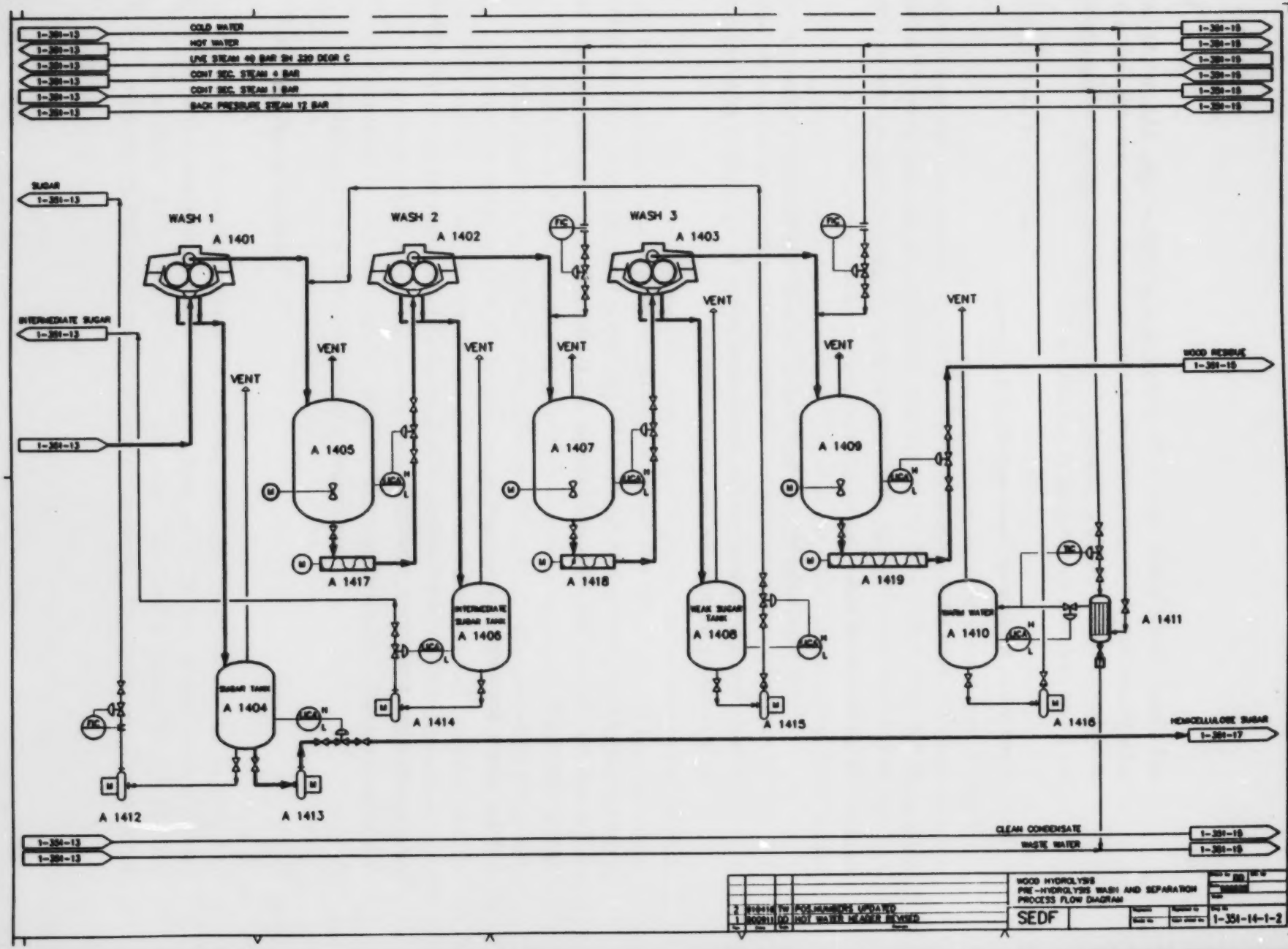
These process steps are depicted on PFD 1-351-14 and are best understood by referring to this PFD and the preceding PFD, 1-351-13, while reading this description.

8.3.1 Roller Presses

A-1401, A-1402, and A-1403 are roller presses which act as a counter-current series of solid-liquid separation devices. Their purpose is to extract the sugar solution, produced during hemicellulose hydrolysis, from the solid cellulose/lignin residue. Solids enter A-1401 from the blow tank, A-1307, shown in the preceding step. Wash water enters tank A-1410, by way of a preheater, for final sugar removal. The flow of water through the series of roller presses is then counter-current to the flow of solids. The sugar concentration in both the solid and liquid leaving each roller press decreases in concentration as the solid residue progresses from A-1401 to A-1402 and finally to A-1403.

8.3.2 Sugar Tanks

The product stream from A-1401, the most concentrated sugar stream, flows to sugar tank A-1404. This tank supplies the hemicellulose sugar to the fermentation section


COLD WATER
HOT WATER
LPS STEAM 40 BAR SH 320 DEGR C
CONT SEC. STEAM 4 BAR
CONT SEC. STEAM 1 BAR
BACK PRESSURE STEAM 12 BAR
SUGAR
INTERMEDIATE SUGAR
WASH 1
A 1401
WASH 2
A 1402
WASH 3
A 1403
VENT
A 1405
A 1407
A 1409
A 1417
A 1418
A 1419
A 1404
A 1406
A 1408
A 1410
A 1411
A 1412
A 1413
A 1414
A 1415
A 1416
WOOD RESIDUE
HEMICELLULOSE SUGAR
CLEAN CONDENSATE
WASTE WATER
WOOD HYDROLYSIS
PRE-HYDROLYSIS WASH AND SEPARATION
PROCESS FLOW DIAGRAM
SEDF
1-351-14-1-2

and a sugar recycle stream back to the prehydrolysis reactor A-1304. The intermediate sugar stream from the second roller press, A-1402, flows back to the first blow tank in the prehydrolysis section (A-1306). This step is part of the counter-current washing scheme, but it also facilitates the transport of the product slurry.

8.3.3 Water Wash, Re-pulping Tanks and Other Equipment

The wash water going to A-1403 is heated with the heat exchange system shown around water tank A-1410 and injected into the feed to the last roller press. The wash water is heated to about the same temperature as the entering feed, in order to effect more efficient washing.

Tanks A-1405, A-1407, and A-1409 are all re-pulping tanks. Their purpose is to mix the wash water or sugar solution with the solids prior to pumping the slurry to the roller presses. Specially designed positive displacement pumps A-1417, A-1418, and A-1419 all serve to convey solids to the next step downstream.

A-1404, A-1406 and A-1408 are sugar tanks involved in the counter-current wash step. Pumps A-1413, A-1414, and A-1415 serve these sugar solution tanks, while A-1416 serves the hot water tank. Additionally, A-1411 is a heat exchanger that serves the hot water tank A-1410.

8.3.4 Sugar Recovery

Theoretical sugar recovery is in excess of 95 per cent with this system (i.e., 95% of the sugar produced is recovered).

8.4 Second Stage (Step 2) Hydrolysis

The second stage hydrolysis process area is shown in PFD 1-351-15.

8.4.1 Feed Preparation

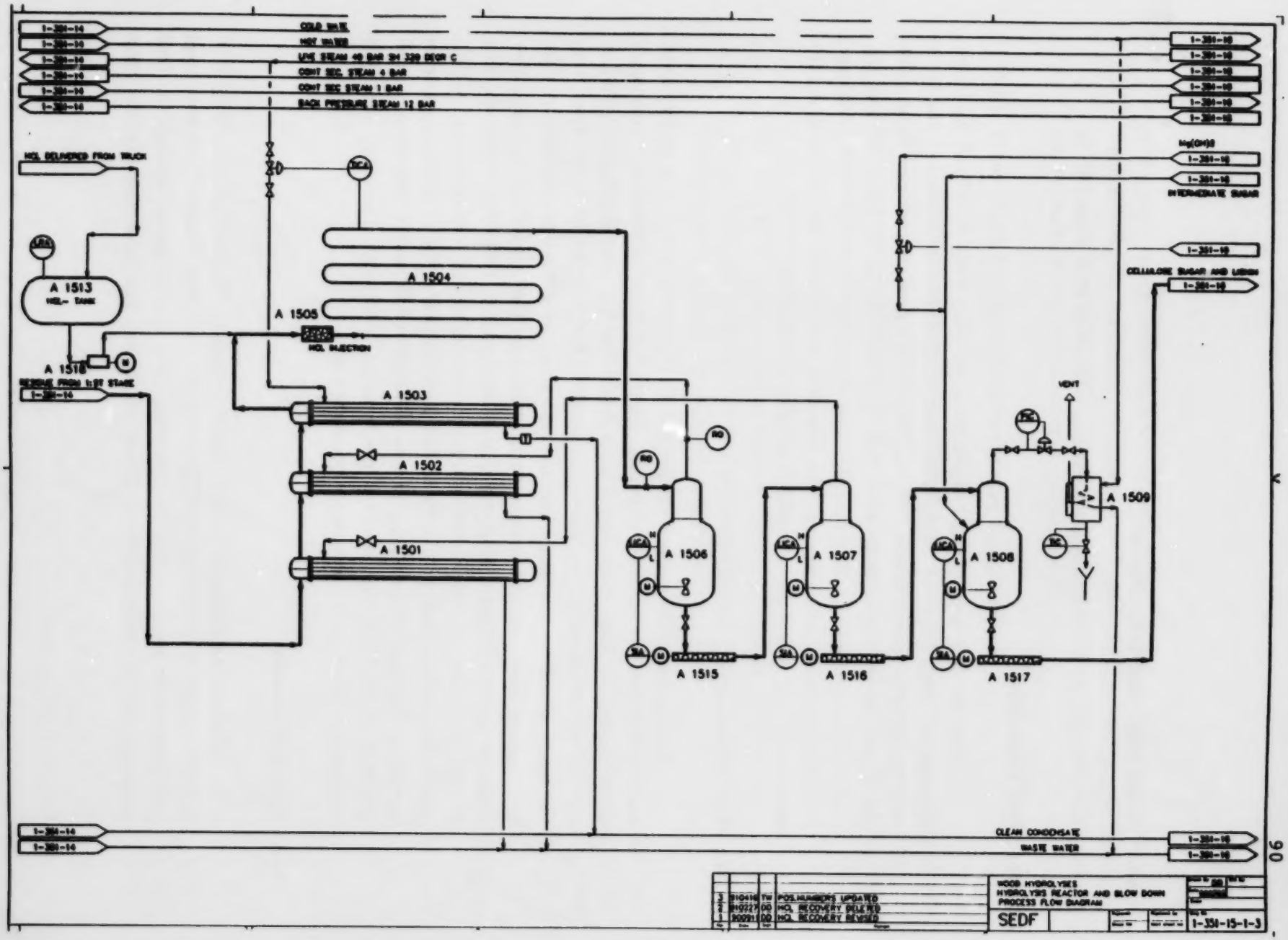
After the final stage of sugar extraction in the roller press A-1403, shown in the preceding section (PFD 1-351-14), the solids containing the unreacted cellulose and lignin are collected in re-pulping tank A-1408, also shown in the preceding section. These solids are diluted in re-pulping tank A-1409 to approximately 20 % (w/v), so that the concentration is suitable for the progressive cavity feed pump A-1419 and the second stage hydrolysis equipment which follows. This re-pulping tank A-1409 and the pump A-1419 serve as the feed system to the second stage (step 2) hydrolysis.

8.4.2 Feed Preheating

Prior to the injection of acid catalyst and the subsequent initiation of the hydrolysis reaction that converts cellulose to glucose, there are a series of three heat exchangers which preheat the feed to the Step 2 Hydrolysis. The first heat exchanger, A-1501, is supplied with flash steam from the second product blow tank, A-1507. The steam from this tank is of lower temperature than the flash steam from the first blow tank, A-1506. Thus, second blow tank flash steam is better utilized for the first preheating (these blow tanks are explained further after the reactor description). Flash steam from the first product blow tank, A-1506, is used as a supply for the second feed preheater, A-1502. This steam (12 bar) is best used in the second preheater, where higher temperature steam is needed. The flashed steam going to both preheater A-1501 and A-1502 contains small quantities of HCl and organics from the hydrolysis reactions. Therefore, after it is condensed it is sent to the wastewater treatment plant.

8.4.3 Hydrolysis Reaction

After exiting preheater A-1502, the feed must be heated further to bring it to reaction temperature (225°C - 230°C). Since all waste heat sources have been used previously, virgin steam is used for this step. The feed is passed through the final preheater, A-1503, which is supplied with 40 bar steam . The condensate from the virgin


COLD WATER
HOT WATER
LOW STEAM 40 BAR 241 220 DEGR C
CONT SEC STEAM 4 BAR
CONT SEC STEAM 1 BAR
BACK PRESSURE STEAM 12 BAR
HCL DELIVERED FROM TRUCK
A 1513
HCL- TANK
A 1518
A 1504
A 1505
HCL INJECTION
A 1503
A 1502
A 1501
A 1506
A 1507
A 1508
A 1509
VENT
A 1515
A 1516
A 1517
INTERMEDIATE SUGAR
CELLULOSE SUGAR AND LIGNIN
CLEAN CONDENSATE
WASTE WATER
WOOD HYDROLYSES
HYDROLYSIS REACTOR AND BLOW DOWN
PROCESS FLOW DIAGRAM
SEDF
1-351-15-1-3
POS.NUMBERS UPDATED
HCL RECOVERY DELETED
HCL RECOVERY REVISED

steam is, of course, clean so it is returned to the steam plant for reuse. Now that the feed is at reaction temperature, the reaction catalyst for the hydrolysis of cellulose to glucose (i.e., HCl) may be injected.

Concentrated (37-40%) hydrochloric acid is stored in storage tank A-1513. After the HCl is injected into the feed stream, via pump A-1518, the mixture passes rapidly through a static mixer unit (A-1505). The thoroughly mixed product passes into the plug flow reactor (A-1504). Because the reaction temperature in the plug flow reactor A-1504 is quite high, the residence time in the reactor is very short, i.e. less than one minute. Because of the short residence time, it is not necessary to provide any additional steam to the plug flow reactor A-1504.

8.4.4 Blow Tanks

The reaction products leave the plug flow reactor A-1504 and travel to a series of three blow tanks. The main purpose of these three blow tanks, A-1506, A-1507, and A-1508, is to reduce the pressure of the reaction product mass so that the solid and liquid phases can be separated and further processed. At the same time, this sequential flashing in three blow tanks allows the recovery of high-grade secondary steam which can be re-used by the process. There are side mount agitators in each of the three blow tanks to prevent solids settling and to ensure exit stream uniformity. There are also mechanical conveying devices A-1515, A-1516, and A-1517, in blow tanks A-1506, A-1507, and A-1508, respectively, to transport the contents of each tank forward.

There are several notable features regarding the blow tanks. The reaction product mass entering blow tank A-1508 is neutralized with $Mg(OH)_2$. The source of the $Mg(OH)_2$ is tank A-1615 shown on PFD 1-351-16. Addition of $Mg(OH)_2$ at this point reduces the corrosiveness of the reaction product mixture as it moves through the downstream equipment. Another feature of the blow tanks is the introduction of intermediate sugar solution into the final blow tank A-1508. This final blow tank (A-1508) serves as the feed tank to the next process step, where sugar extraction is performed. The source of the intermediate sugar is tank A-1609 shown on PFD 1-351-16. $Mg(OH)_2$ can also be added to blow tank A-1508 for final pH adjustment.

8.4.5 Blow Tank Exhaust Steam

As previously explained, the flash steam from the first blow tank (A-1506) is the heat source for the second preheater (A-1502). The flash steam from the second blow tank, A-1507, is the supply for the first preheater, A-1501. This configuration is chosen to make the best match between the temperatures and quantities of heat in different waste steam sources and the heat requirements of the preheat system. The flash steam from the final blow tank A-1508 is not of sufficient quality to be reused. This steam travels to condenser A-1509. The condensed steam leaving A-1509 contains small quantities of HCl and organics and thus, it is sent to the wastewater treatment plant.

8.5 Step 2 Hydrolysis Separation/Washing

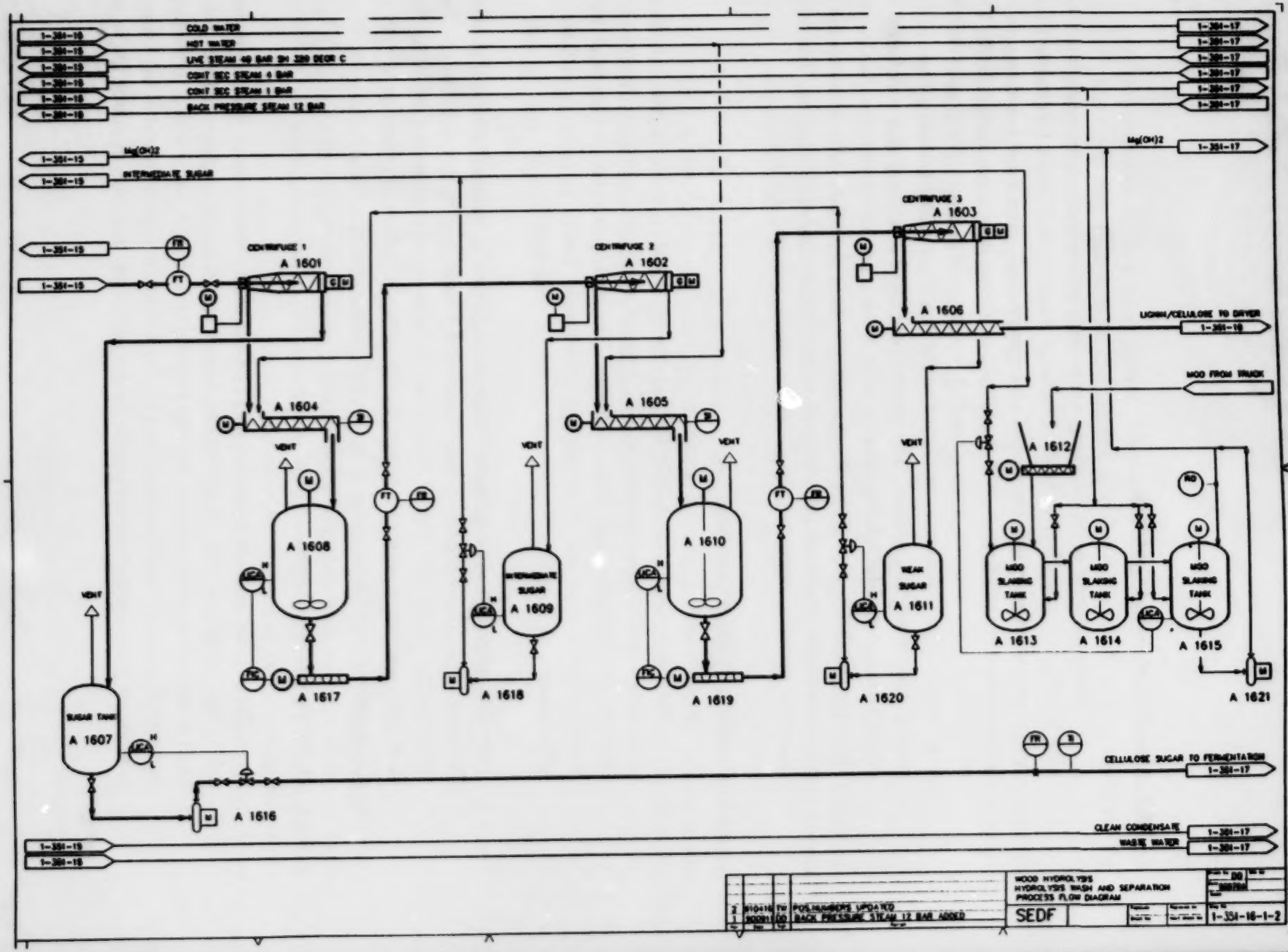
The separation/washing steps for the product of second stage hydrolysis are depicted in PFD 1-351-16.

8.5.1 Use Of Three Centrifuges

After the final wood hydrolysis step, sugar is separated from the lignin and unreacted cellulose by counter-current washing with three decanter-centrifuges in series. The sugar stream from the first centrifuge (A-1601) is pumped to the fermentation section. Fresh water is only added to the feed of the last centrifuge in the series.

8.5.2 Operation Of First Centrifuge

The first centrifuge A-1601 is fed by pump A-1517 (shown on the preceding PFD). The solids from centrifuge A-1601 pass to mixing conveyor A-1604 where the liquid overflow (i.e., weak sugar solution) from the last centrifuge is added. The resultant mixture is pumped to the second centrifuge in the train. The overflow stream from centrifuge A-1601 is received by tank A-1607. This is the second-stage sugar product tank, which supplies the cellulose hydrolysate portion of the fermentation medium.


COLD WATER
HOT WATER
LIVE STEAM 40 BAR SH 320 DEGR C
CONT REC STEAM 4 BAR
CONT REC STEAM 1 BAR
BACK PRESSURE STEAM 12 BAR
Mg(OH)2
INTERMEDIATE SUGAR
CENTRIFUGE 1
A 1601
CENTRIFUGE 2
A 1602
CENTRIFUGE 3
A 1603
A 1604
A 1605
A 1606
LIGNIN/CELLULOSE TO DRYER
WOOD FROM TRUCK
A 1607
A 1608
A 1609
A 1610
A 1611
A 1612
A 1613
A 1614
A 1615
A 1616
A 1617
A 1618
A 1619
A 1620
A 1621
VENT
CELLULOSE SUGAR TO FERMENTATION
CLEAN CONDENSATE
WASTE WATER
WOOD HYDROLYSIS
HYDROLYSIS WASH AND SEPARATION
PROCESS FLOW DIAGRAM
SEDF
1-351-16-1-2
BACK PRESSURE STEAM 12 BAR ADDED

8.5.3 Operation of Second Centrifuge

Mixing conveyor A-1604 discharges to holding tank A-1608, which serves as the feed tank for the next centrifuge A-1602. Discharge pump A-1617 serves holding/feed tank A-1608 and supplies feed to the second centrifuge A-1602. The liquid overflow product from the second centrifuge A-1602 is collected in intermediate sugar tank A-1609. This intermediate sugar solution is transferred to two different points by pump A-1618. The intermediate sugar solution is transferred to the final blow tank (A-1508) as part of the counter-current washing scheme. The intermediate sugar solution is also transferred via pump A-1618 to the MgO slaking tank (A-1613) which is part of the neutralization system. The sugar solution is used in the slaking operation both to reduce water consumption in the process and to maximize sugar concentration in the product sugar solution. The solids underflow from centrifuge A-1602 proceed to mixing conveyor A-1605.

8.5.4 Operation Of Third Centrifuge

Hot water from tank A-1410 (PFD 1-351-14) is added to the A-1602 centrifuge solids underflow in mixing conveyor A-1605. The hot water tank A-1410 also supplies hot water for the first-stage sugar separation step. The mixing conveyor A-1605 feeds tank A-1610, which is again both a holding and a feed tank. Discharge pump A-1619 serves holding/feed tank A-1610 and is the feed pump for centrifuge A-1603.

The solids underflow from centrifuge A-1603 flows to transport conveyor A-1606. The unreacted cellulose/lignin is then transferred forward for further processing. The liquid overflow from centrifuge A-1603 is sent to weak sugar storage tank A-1611. This weak sugar solution is added via pump A-1620 to the underflow of centrifuge A-1601 in mixing conveyor A-1604.

8.5.5 Magnesium Oxide Slaking

Three tanks and one solids bin comprise the main components of the magnesium oxide (MgO) slaking system. Solid MgO is received and stored in solids bin A-1612. Solid MgO is metered from bin A-1612 into MgO slaking tank A-1613, along with intermediate sugar solution transferred from tank A-1609. Sugar solution is used instead of fresh water to minimize process water requirements. At the same time, this helps maximize the sugar

concentration in the product stream. One bar steam is added as needed to dissolve the MgO in slaking tank A-1613. An agitator is included in tank A-1613 to accelerate the dissolution of MgO.

From slaking tank A-1613, the $Mg(OH)_2$-sugar solution flows to tank A-1614 for additional residence time. One bar steam can be added to this tank as needed and again, there is an agitator to facilitate MgO-water mixing.

8.5.6 Use Of Magnesium Hydroxide

The final tank in the MgO slaking system is A-1615. $Mg(OH)_2$/ sugar solution is pumped from tank A-1614 to tank A-1615. One bar steam can also be added to tank A-1615 if needed.

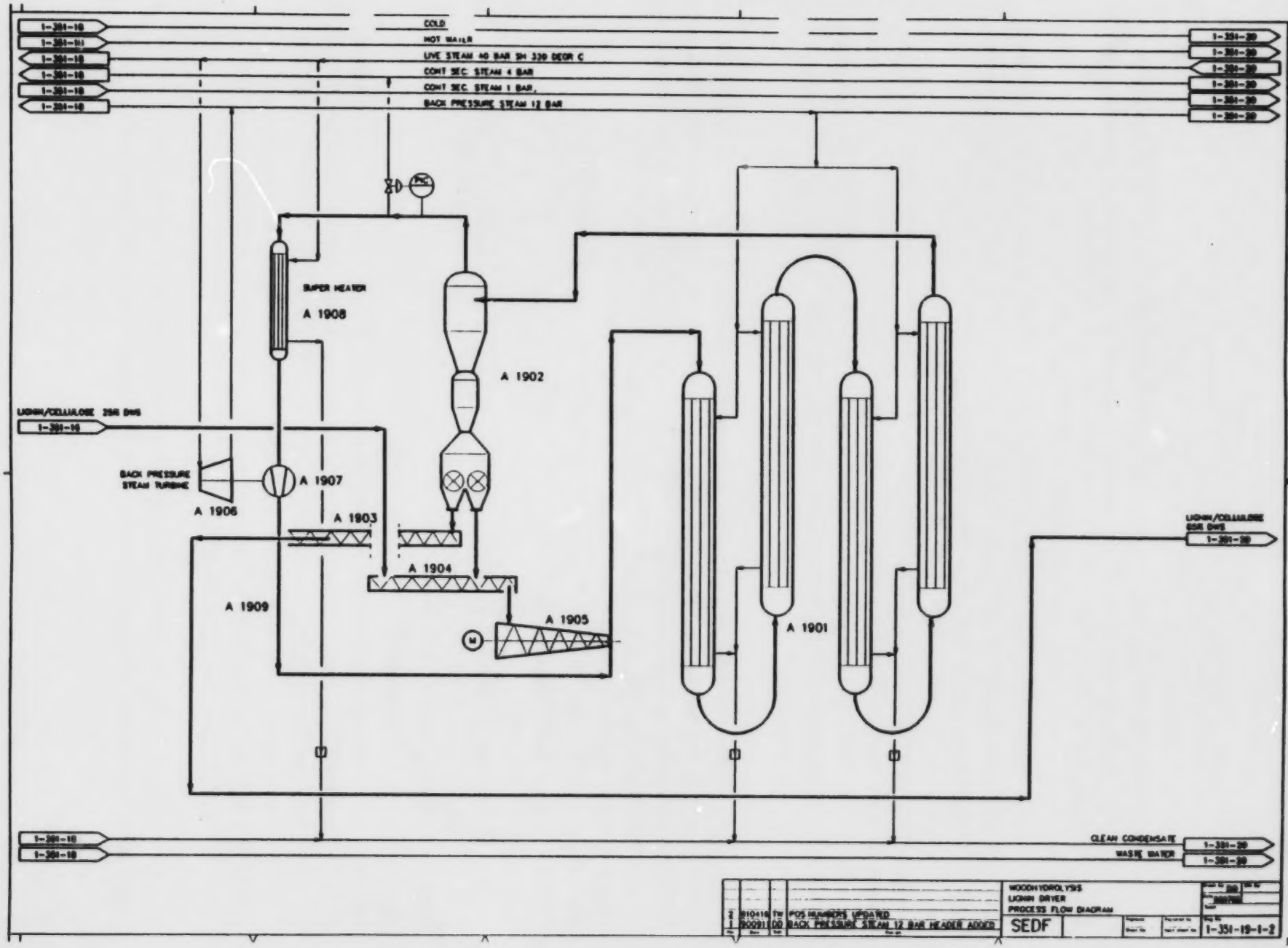
The final $Mg(OH)_2$ solution is transferred via pump A-1621 to blow tanks A-1506 and A-1508 (shown on PFD 1-351-15) for neutralization. The $Mg(OH)_2$ solution is also transferred to sugar storage tank A-1701 (as shown on PFD 351-17) where any necessary final pH adjustments can be made before fermentation.

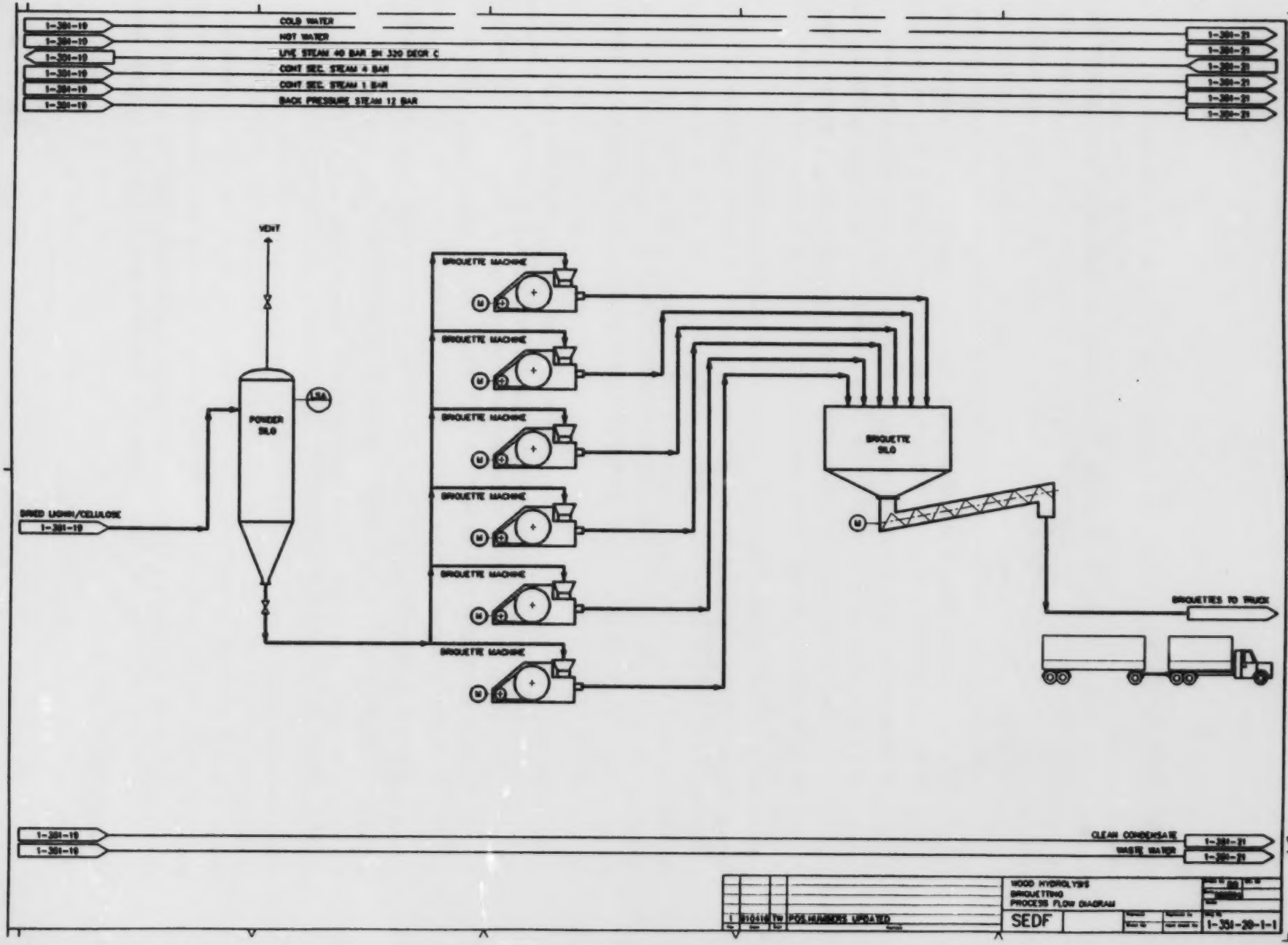
8.6 Lignin Drying Section

The process equipment included in the lignin drying is shown in PFD 1-351-19.

8.6.1 Feed System

The lignin and residual cellulose enter conveyor A-1904. This lignin and unreacted cellulose has previously been processed at the hydrolysis wash and separation step where the sugar was removed. At conveyor A-1904, dried lignin/cellulose is added to this fresh feed to make up the solid feed to lignin dryer A-1901. Conveyor A-1904 discharges into plug screw A-1905, which serves as a pressure lock between the solids feed system and the back pressure from lignin dryer A-1901.


COLD
HOT WATER
LIVE STEAM 40 BAR SH 320 DEGR C
CONT SEC STEAM 4 BAR
CONT SEC STEAM 1 BAR,
BACK PRESSURE STEAM 12 BAR
SUPER HEATER
A 1908
A 1902
A 1907
A 1906
A 1903
A 1904
A 1905
A 1909
A 1901
CLEAN CONDENSATE
WASTE WATER
WOODHYDROLYSIS
LIGNIN DRYER
PROCESS FLOW DIAGRAM
SEDF
1-351-19-1-2


1-351-19
COLD WATER
1-351-19
HOT WATER
1-351-19
LP/IP STEAM 40 BAR SH 320 DEGR C
1-351-19
CONT SEC. STEAM 4 BAR
1-351-19
CONT SEC. STEAM 1 BAR
1-351-19
BACK PRESSURE STEAM 12 BAR
1-351-21
1-351-21
1-351-21
1-351-21
1-351-21
1-351-21
VENT
LSA
POWDER SILO
DRIED LIGNIN/CELLULOSE
1-351-19
BRIQUETTE MACHINE
BRIQUETTE MACHINE
BRIQUETTE MACHINE
BRIQUETTE MACHINE
BRIQUETTE MACHINE
BRIQUETTE MACHINE
BRIQUETTE SILO
BRIQUETTES TO TRUCK
1-351-19
1-351-19
CLEAN CONDENSATE
WASTE WATER
1-351-21
1-351-21
1 210486 TW POS. NUMBERS UPDATED
WOOD HYDROLYSIS
BRIQUETTING
PROCESS FLOW DIAGRAM
SEDF
1-351-20-1-1

8.6.2 Dryer Operation

Plug screw A-1905 discharges into a stream which contains steam recycled from lignin dryer A-1901. This mixture of steam and solid material is then fed to lignin dryer A-1901. The lignin dryer (A-1901) consists of a series of four tube and shell heat exchangers. The material to be dried travels through the tubes in series. Twelve bar steam is supplied to the shell side of each of the four heat exchangers that constitute the dryer. This 12 bar steam is supplied from the discharge of back pressure steam turbine A-1906. While the material to be dried is fed through the four heat exchangers in series, the steam is fed in parallel. The condensate from lignin dryer A-1901 is clean and is returned to the steam generation plant for re-use. The dried product from lignin dryer A-1901 exits the last of the four heat exchangers that constitute dryer and flows, with its conveying steam, to cyclone system A-1902. Dried material from the cyclone is briquetted as outlined in PFD 1-351-20.

8.6.3 Product Discharge

There are three different discharge streams from cyclone system A-1902. There are two solids discharges. One of these carries dried product which is transported from the system via conveyor A-1903.

The other solid discharge provides dried material for recycle, as previously mentioned in the description of the incoming feed conveyor A-1904. The third discharge is steam which flows to super heater A-1908. On the way to super heater A-1908, part of this steam is withdrawn in a quantity equal to the amount of water contained in the incoming fresh lignin/cellulose feed. This steam, at a pressure of 4 bar, is contaminated and is used elsewhere in the factory, mainly in the distillation plant.

8.6.4 Steam Recycle and Energy Economy

Super heater A-1908 is a tube and shell heat exchanger with a heating medium of 40 bar steam on the shell side. The condensate from this 40 bar steam is clean, and it travels, with the condensate from the lignin dryer, to the steam generation plant for re-use. The steam entering the tube side of super heater A-1908 is live, superheated steam directly from the high pressure boiler. After the recycled steam is reheated in super heater

A-1908, it is compressed to dryer-operating pressure (12 bar) with compressor A-1907. Compressor A-1907 is driven by back pressure steam turbine A-1906. The use of steam turbine A-1906, which is fed with superheated 40 bar steam, is important both to the heat economy in this system and the total energy economy. As previously mentioned, the exhaust steam from steam turbine A-1906, which is at 12 bar, supplies heat to the lignin dryer and the first stage reactor.

8.7 Fermentation Section

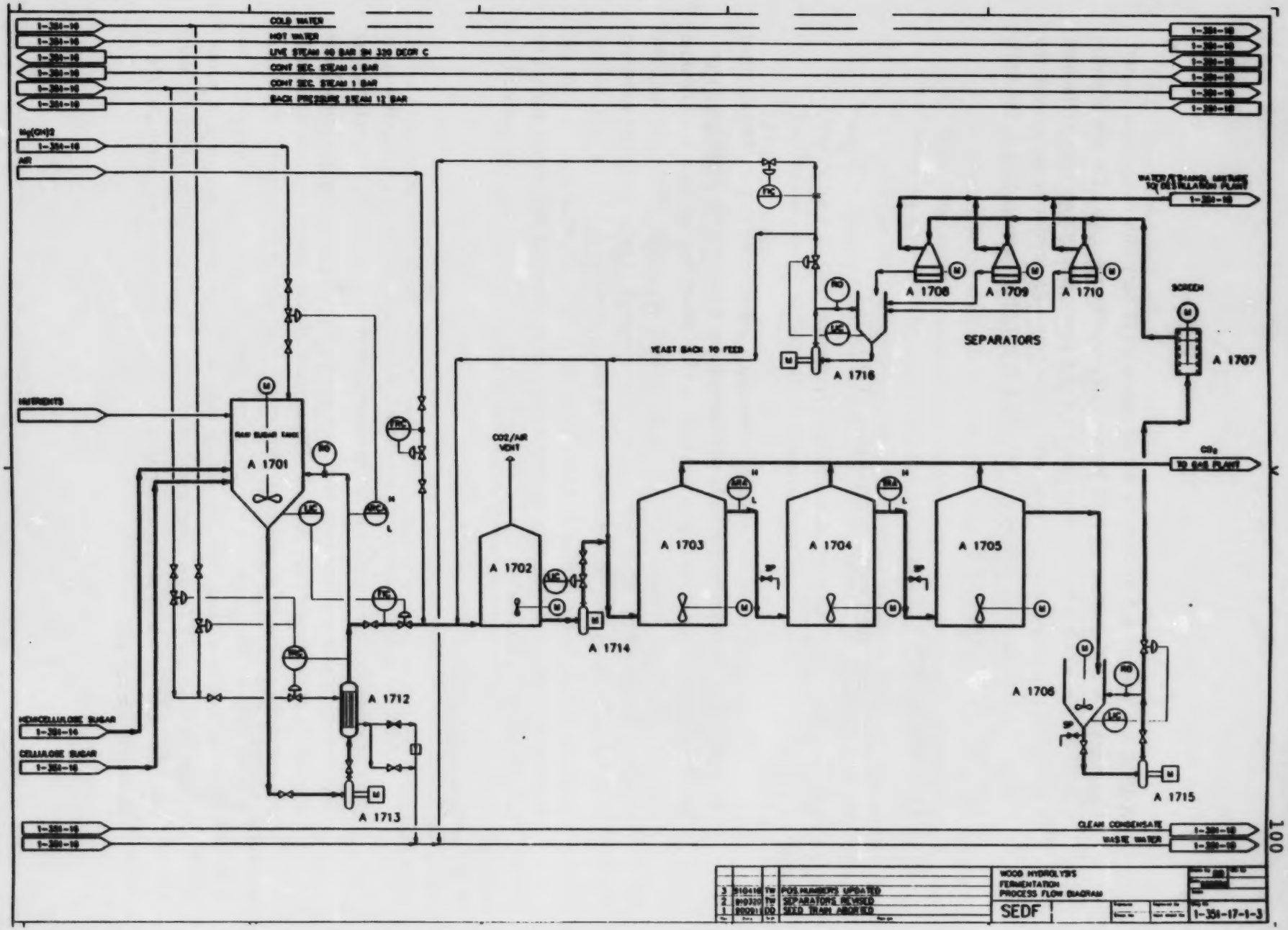
The fermentation system is depicted in PFD 1-351-17.

8.7.1 Preparation of Substrate

The system depicted is a cascade fermentation system in which the substrate flows through a series of fermentation tanks with the ethanol concentration increasing in each successive tank. The process begins with tank A-1701, which receives both hemicellulose and cellulose sugar streams. The two sugar streams are mixed. Nutrients and any $Mg(OH)_2$ needed for pH adjustment, are added at this point. The fermentation substrate is circulated through heat exchanger A-1712 by means of pump A-1713. Either one bar steam or cooling water is used in heat exchanger A-1712, to either heat or cool the fermentation substrate. Generally, heating is required in the winter and cooling is required in the summer to achieve the desired fermentation temperature of approximately 30°C.

8.7.2 Prefermentation

After the proper temperature is achieved, the required nutrients are added, and the pH is adjusted, the fermentation substrate is transferred via pump A-1713 to prefermenter tank A-1702. Yeast is added from seed tank A-1716 only during system start-up. Yeast is grown in prefermenter tank A-1702. The amount of yeast grown represents about 20 percent of the total yeast requirement. Most of the yeast used in fermentation is recycled; the only makeup required is that to replace dead yeast. Because the growth is carried out under aerobic conditions, the gas exiting tank A-1702 is mostly air, so it is vented separately from the CO_2 gas generated downstream. The fermentation substrate, along with the yeast grown in prefermenter tank A-1702, is transferred via pump A-1714 to fermenter tank A-1703.



3	910416	TW	POS NUMBERS UPDATED	
2	910320	TW	SEPARATORS REVISED	
1	910211	DD	SEED TRAIN ADDED	

WOOD HYDROLYSIS
FERMENTATION
PROCESS FLOW DIAGRAM

SEDF

1-351-17-1-3

8.7.3 Fermentation

The fermentation substrate is mixed with recycled yeast from the yeast separators (A-1708, A-1709, and A-1710) as it is pumped to fermenter tank A-1703.

Care is taken to exclude air from the fermenter tank since, as previously mentioned, the fermentation of sugar to ethanol is an anaerobic process. Yeast converts sugar to ethanol and carbon dioxide (CO_2) in approximately equal quantities (by weight). Thus, the off-gas from fermenter tank A-1703 is mostly CO_2. The CO_2 is collected in a common pipe from all fermenters except tank A-1702. The CO_2 can either be vented to the atmosphere or used for purposes such as beverage manufacture. Fermenter tanks A-1704 and A-1705 have the same features as described for fermenter tank A-1703. The ethanol concentration increases as the fermentation substrate progresses from one tank to the next. The substrate enters the bottom of each fermenter tank and exits from the top. There are sample ports between fermenter tanks A-1703 and A-1704, and again between A-1704 and A-1705, as shown on the PFD. After the final fermenter tank A-1705, the fermentation is complete, and the substrate is now referred to as beer.

8.7.4 Beer/Yeast Separation

The beer flows from the top of the final fermenter tank A-1705 to a pump suction tank, A-1706. The beer is transported from tank A-1706 via pump A-1715 to screen A-1707. Screen A-1707 removes coarse, foreign material from the beer and then the beer (which contains yeast) passes to the centrifuges (one is a maintenance stand-by centrifuge). The solid underflow (yeast) flows from the bottom of each of the three centrifuges and is combined in tank A-1716. The yeast collected in tank A-1716 is recycled back to the first fermenter (A-1703). The overflow or clarified beer goes to the distillation plant. Note that it is also possible to transport this yeast via pump A-1717 to a takeoff point where the yeast can be withdrawn for another use, such as for animal feed. In unusual circumstances, such as contamination of the yeast, it may be withdrawn and disposed of.

8.8 Ethanol Distillation Section

The distillation process steps are depicted in PFD 1-351-18.

8.8.1 Beer Storage

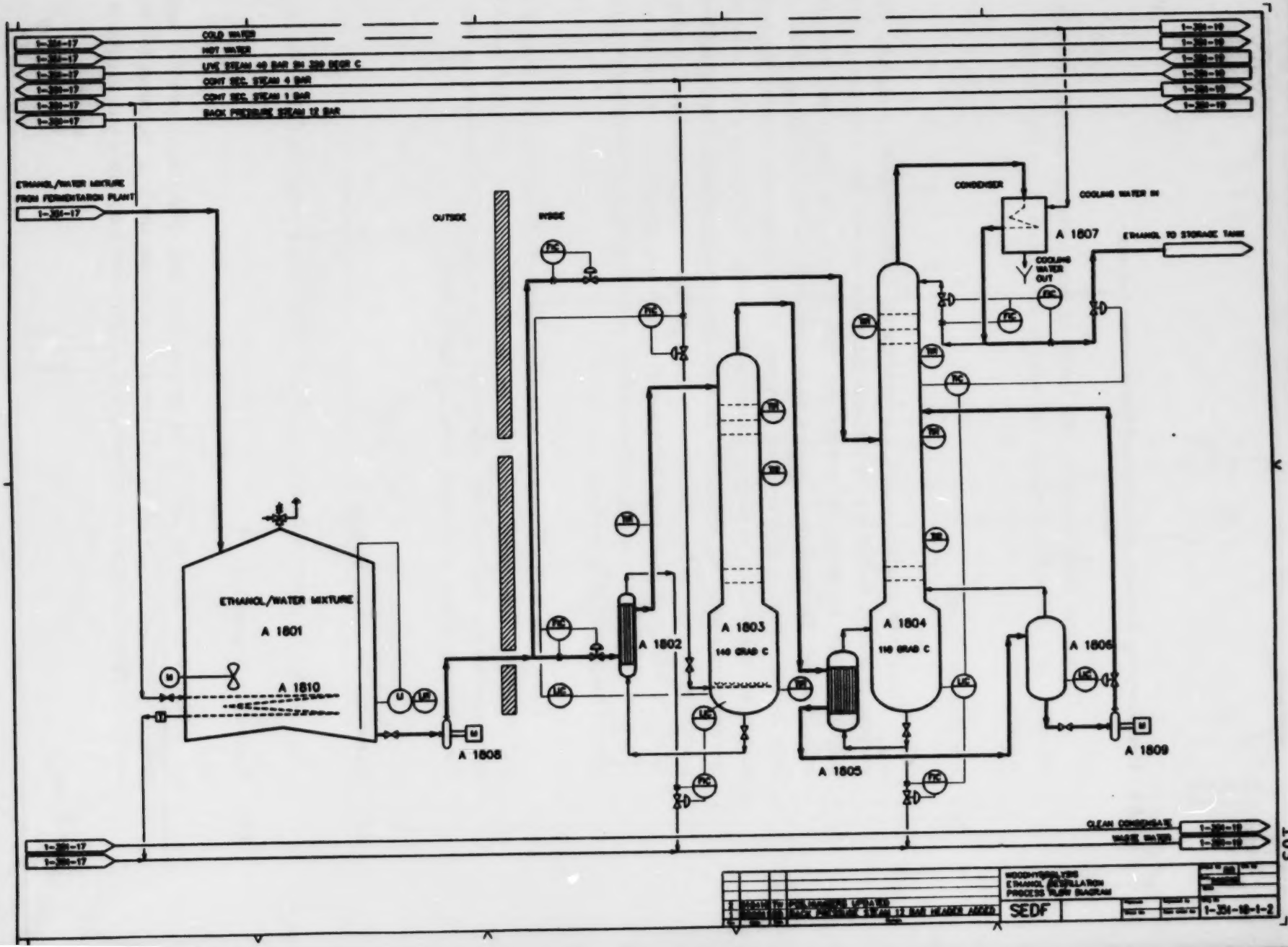
Clarified beer from the fermentation section enters ethanol/water tank A-1801 . Tank A-1801 is equipped with a steam coil which is supplied with one bar steam to prevent freezing of the ethanol/water mixture (beer) during cold weather (the ethanol content of the beer is relatively low at about four percent and the beer could conceivably freeze). Tank A-1801 is also equipped with an agitator for internally circulating the beer. This internal circulation helps with heat transfer but its main purpose is to keep suspended solids in the beer from settling to the bottom of tank A-1801. These suspended solids would most likely be fine yeast particles which have passed through the clarification step in the fermentation section. There is a vent system on the top of tank A-1801 to permit gases to exhaust as the beer is pumped into tank A-1801 from the fermentation section or enter the tank when beer is pumped from it.

8.8.2 Preheating Feed to Stripping Column

Pump A-1808 serves as the feed pump to the distillation system. It transfers beer from tank A-1801 to heat exchanger A-1802. As the beer passes through heat exchanger A-1802, it is preheated using waste heat in the water from the bottoms stream of the first distillation column. This water is thus cooled before being pumped to waste treatment.

8.8.3 Operation Of Stripping Column

From heat exchanger A-1802 the preheated beer flows to the top of the first of a series of two distillation columns. This column, A-1803, is a conventional ethanol stripping column. The purpose of stripping column A-1803 is to separate the majority of the ethanol from the water in the beer. Although the beer has been preheated, it is necessary to add more heat to stripping column A-1803. Thus, live four bar steam is sparged into the bottom of the stripping column.


COLD WATER
HOT WATER
LIVE STEAM 40 BAR SH 320 DEGR C
CONT SEC. STEAM 4 BAR
CONT SEC. STEAM 1 BAR
BACK PRESSURE STEAM 12 BAR
ETHANOL/WATER MIXTURE
FROM FERMENTATION PLANT
OUTSIDE
INSIDE
CONDENSER
COOLING WATER IN
A 1807
ETHANOL TO STORAGE TANK
COOLING WATER OUT
ETHANOL/WATER MIXTURE
A 1801
A 1810
A 1802
A 1803
140 GRAD C
A 1804
140 GRAD C
A 1805
A 1806
A 1808
A 1809
CLEAN CONDENSATE
WASTE WATER
WOODHYDROLYSE
ETHANOL DISTILLATION
PROCESS FLOW DIAGRAM
SEDF
1-351-10-1-2

8.8.4 Heat Economy Between Stripping and Rectification Columns

The vapour from column A-1803 travels to heat exchanger A-1805, which is a reboiler. As it condenses, it reheats the water at the bottom of the second distillation column.

8.8.5 Rectification Column

This second column, A-1804, is a conventional ethanol rectification column. The purpose of column A-1804 is to concentrate the weaker ethanol feed from the stripping column A-1803 to about 95 volume per cent ethanol (the azeotropic limit for ethanol/water). The condensed vapour from heat exchanger A-1805 flows to accumulation tank A-1806. Tank A-1806 is served by pump A-1809 which then supplies the main amount of ethanol/water to rectifier column A-1804. Note that there is a feed point for unstripped beer below the entrance of the main ethanol/water mixture. Unstripped beer is added at this point as part of the heat economy practised during distillation. It is added below the main feed point since it is lower in ethanol concentration (the most efficient distillation is obtained by adding feed to a column at the column point which has the same ethanol concentration as the feed.

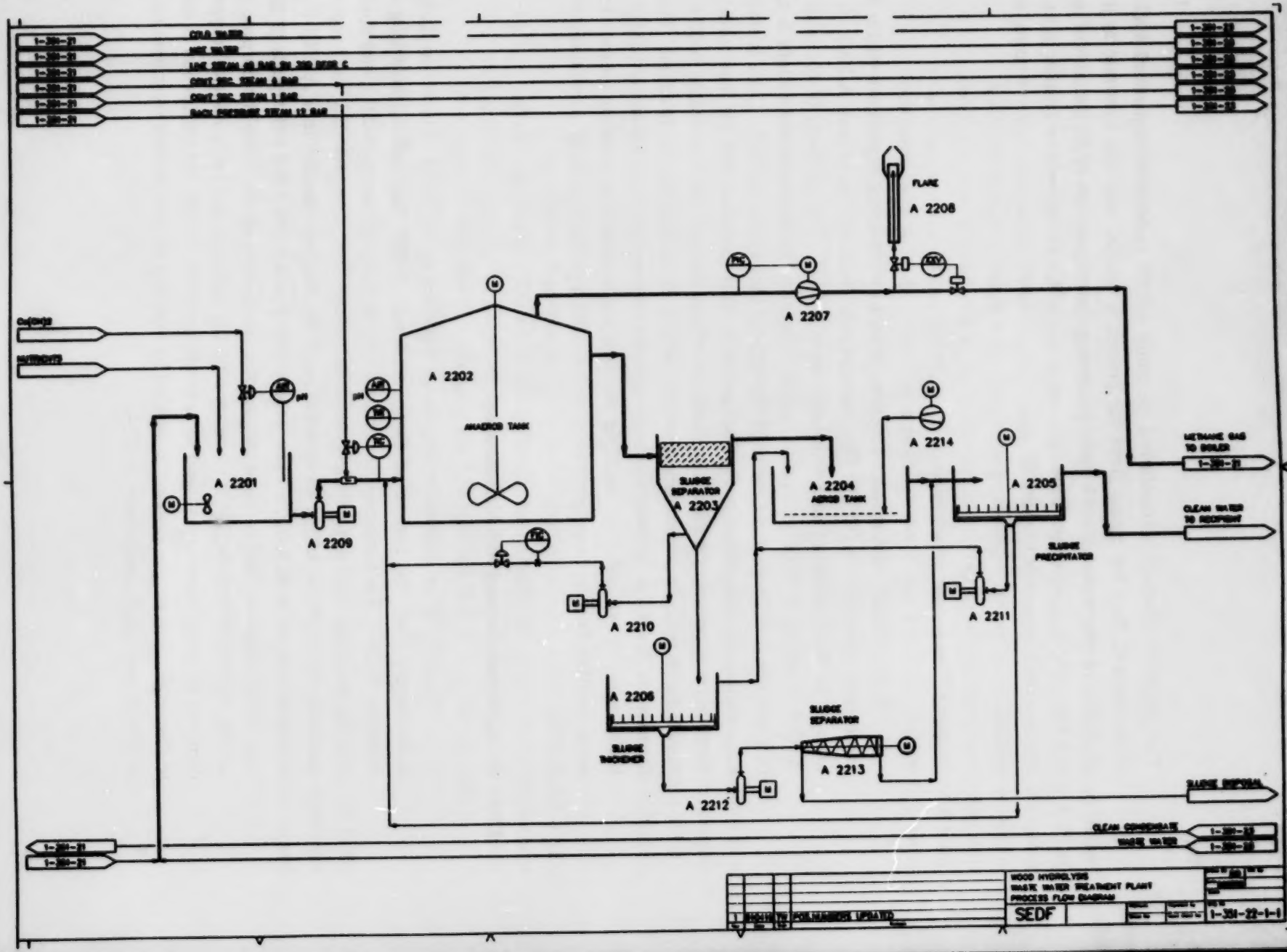
The vapour leaving the top of the rectifier column A-1804 contains 95 volume per cent ethanol. This vapour is condensed in the water-cooled condenser A-1807. Approximately one quarter of the condensed 95 per cent ethanol is withdrawn as product. The remaining ethanol is returned to the column as reflux.

8.9 Wastewater Treatment Section

The CASH plant's wastewater treatment facility is represented in PFD 1-351-22.

8.9.1 Wastewater Preparation

Wastewater from all parts of the process flows into collection/preparation tank A-2201. Lime ($Ca(OH)_2$) is added to the water to neutralize any acid. Nutrients for the subsequent fermentation are also added to tank A-2201 which is equipped with an agitator.


FLARE
A 2208
A 2207
A 2202
ANAEROB TANK
A 2201
A 2209
SLUDGE SEPARATOR A 2203
A 2204 AEROB Tank
A 2214
A 2205
METHANE GAS TO BOILER
CLEAN WATER TO RECIPIENT
SLUDGE PRECIPITATOR
A 2211
A 2210
A 2206
SLUDGE THICKENER
SLUDGE SEPARATOR
A 2213
A 2212
SLUDGE DISPOSAL
CLEAN CONDENSATE
WASTE WATER
WOOD HYDROLYSIS
WASTE WATER TREATMENT PLANT
PROCESS FLOW DIAGRAM
SEDF
1-304-22-1-1

The prepared substrate is transferred via pump A-2209 to fermentation vessel A-2202. Contaminated, four bar steam from the process is injected into this substrate as it is transferred to fermenter A-2202, thereby elevating the temperature of the contents of tank A-2202 to the proper temperature for fermentation. Recycle streams from other parts of the wastewater treatment facility are also injected into the wastewater as it travels to tank A-2202.

8.9.2 Methane Generation

Tank A-2202 operates under anaerobic conditions converting organic material in the wastewater into methane (CH_4). The methane exits from the top of tank A-2202. It is brought to the desired pressure with compressor A-2207. The discharge of compressor A-2207 is sent to a steam generation boiler. There is a pressure control system in the methane line that bleeds some methane through the flare system A-2208. There is always some methane flowing through the flare system A-2208 to ensure that the flare stays lit. However, it is possible for all of the methane to pass through the flare system A-2208 if the discharge valve in the methane line downstream of the flare system is closed. Thus, flare system A-2208 is designed to ensure that the methane generated is safely burned if boiler demands are such that not all of the methane is needed to generate steam. The water overflow from methane generation tank A-2202 is pumped to sludge separation tank A-2203.

8.9.3 Sludge Separation and Aerobic Treatment

There are three streams leaving sludge separator tank A-2203. Thickened sludge is discharged from the bottom of sludge separator A-2203 for further processing in thickener A-2206. Methanogenic bacteria are recycled through pump A-2210, and mixed with the incoming feed to methane generation tank A-2202, thus providing the bacteria needed in this tank. Clarified water overflows from sludge separation tank A-2203 into aerobic treatment tank A-2204. Two other streams which are from other parts of the wastewater treatment facility, also enter aerobic treatment tank A-2204. The purpose of aerobic treatment tank A-2204 is to satisfy both the chemical and bacteriological oxygen demands of waste material not used to generate methane, so that the wastewater is safe to discharge. This oxygen demand is satisfied by injecting air into aerobic treatment tank A-2204 by way of air compressor A-2214.

8.9.4 Sludge Thickener

The sludge that settles in the bottom of sludge separator A-2203 drains to sludge thickener A-2206. There is a slow-moving rake in the bottom of sludge thickener A-2206, as exists in most conventional thickeners. The sludge that settles is transferred via pump A-2212 to sludge separator A-2213. The sludge is further concentrated in sludge separator A-2213, a conventional centrifuge. The more concentrated sludge is taken to landfill, and the water separated from this sludge is combined with the water overflow from aerobic treatment tank A-2204. The other stream leaving sludge thickener A-2206 is a water overflow stream which is sent to aerobic treatment tank A-2204.

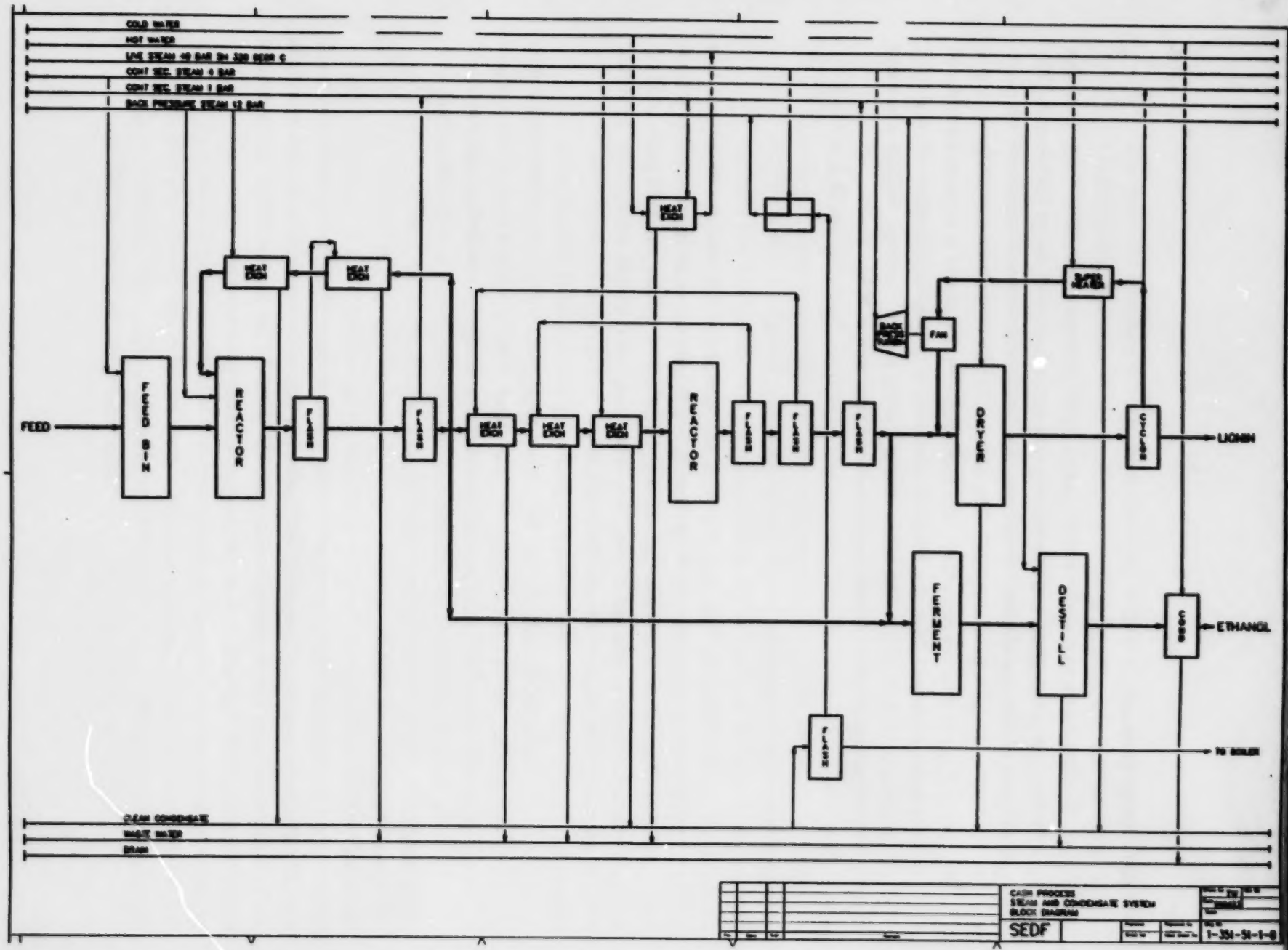
8.10 Steam Generation Plant

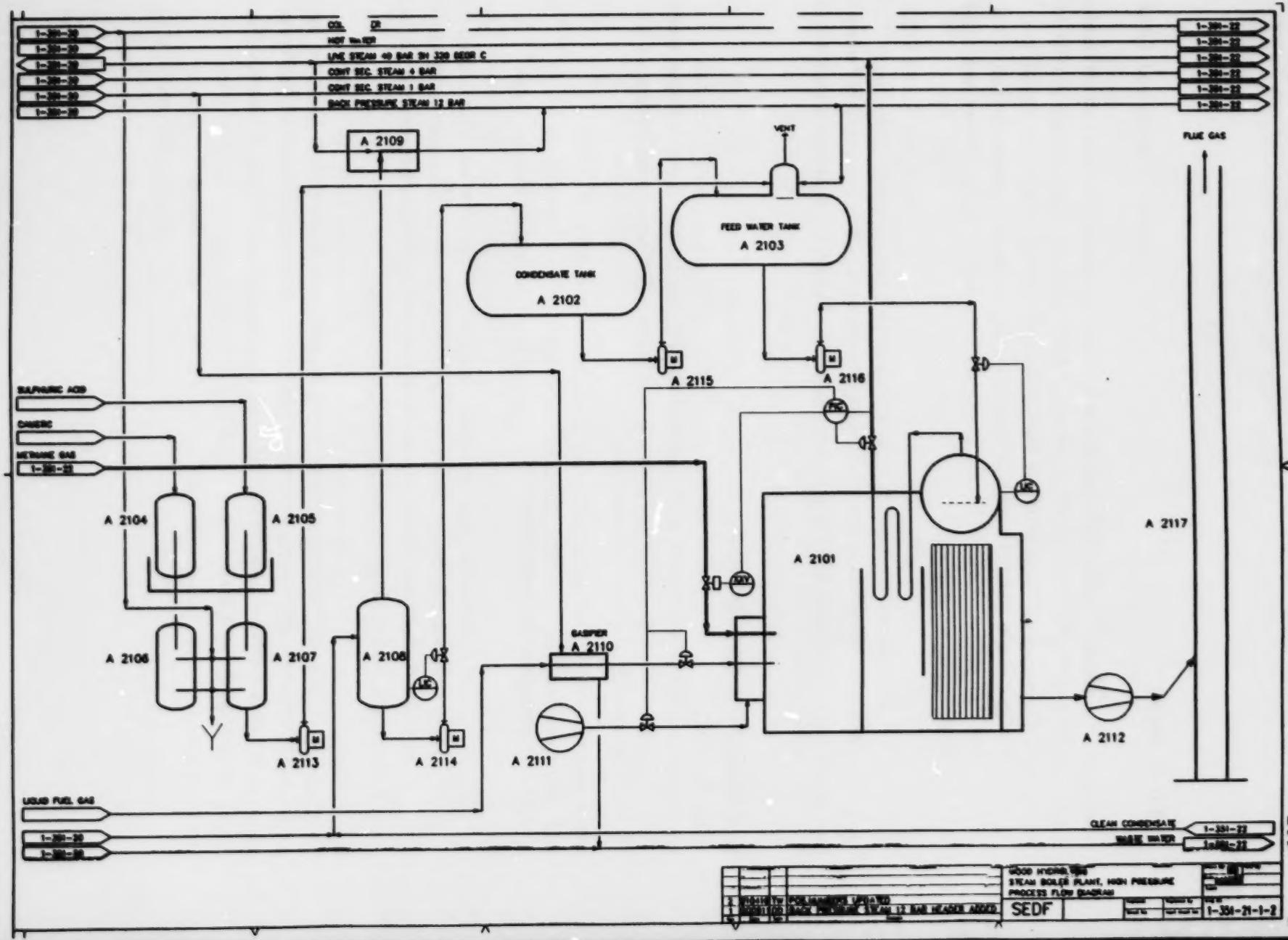
The following is an explanation of the total steam and condensate systems in a CASH plant and is best understood from an overall perspective by referring to the process block diagram 1-351-00, and the steam and condensate system block diagram 1-351-51. Because these systems encompass the entire plant, one should refer to the individual process flow diagrams for specific details.

The systems described are for a stand-alone plant without integration with a pulp mill or other facility. The stand-alone plant utilizes a boiler which is fuelled with methane generated within the CASH process. This methane is supplemented with purchased fuels. The boiler is not limited to methane; any fuel, gaseous, liquid, or solid will suffice.

8.10.1 High Pressure Steam

Steam, at a pressure of 40 bar and a temperature of 320°C, is generated by boiler A-2101 shown on PFD 1-351-21 . This steam is used in drying and second stage hydrolysis, and to boost the pressure of steam supplied to the 12 bar header. Much of the exhaust steam from high pressure steam use goes to other process steps.


COLD WATER
HOT WATER
LIVE STEAM 40 BAR SH 320 DEGR C
CONT SEC. STEAM 4 BAR
CONT SEC. STEAM 1 BAR
BACK PRESSURE STEAM 12 BAR
FEED
LIQUID S-H
REACTOR
HEAT EXCH
FLASH
REACTOR
FAN
DRYER
CYCLONE
LIGNIN
FERMENT
DISTILL
COOL
ETHANOL
TO BOILER
CLEAN CONDENSATE
WASTE WATER
DRAIN
CASH PROCESS
STEAM AND CONDENSATE SYSTEM
BLOCK DIAGRAM
SEDF
1-351-51-1-0


A 2109
VENT
FEED WATER TANK
A 2103
CONDENSATE TANK
A 2102
A 2115
A 2116
FLUE GAS
A 2117
A 2104
A 2105
A 2101
A 2106
A 2107
A 2108
BARRIER
A 2110
A 2113
A 2114
A 2111
A 2112
SEDF
STEAM BOILER PLANT, HIGH PRESSURE
PROCESS FLOW DIAGRAM
1-351-21-1-2

8.10.1.1 Drying

The boiler steam which is generated at 40 bar is used to operate steam turbine A-1906 and super heater A-1908 as shown on PFD 1-351-19. Using turbine A-1906 instead of an electric motor reduces the plant electrical needs by approximately 750 kw. This energy efficient back pressure turbine supplies the turbine requirement for the drying step and then exhausts clean 12 bar steam into the intermediate steam pressure header for use in other process sections.

Contaminated steam at 4 bar is exhausted from the dryer cyclone A-1902. This steam goes into a header for use in other process areas. There is some 40 bar steam used for indirect heating that is completely condensed. The clean condensate is returned to the steam plant.

8.10.1.2 Second Stage Hydrolysis

Plug flow reactor A-1503 shown on PFD 1-351-15 is supplied 40 bar steam for indirect heating. All of this steam is condensed. The clean condensate goes into the header for return to the steam plant.

8.10.2 Intermediate Pressure Steam

The intermediate pressure steam header is at 12 bar pressure. This is clean steam, mainly supplied from back pressure turbine A-1906. However, this header is also supplied by steam flashed from the condensate collection system. This flashed steam is mixed with sufficient 40 bar steam to raise its pressure to 12 bar.

This intermediate pressure steam is used only at reactor A-1304 and at heat exchanger A-1301, during first stage hydrolysis (as shown in PFD 1-351-13). Part of this steam is condensed and re-used as clean condensate and part goes to the one bar contaminated steam header.

8.10.3 Low Pressure Steam

There are two low pressure steam systems. One system operates at 4 bar pressure and the other at 1 bar. The steam in both systems is steam exhausted from the process and is thus contaminated. Any condensate resulting from the use of either of the low pressure steams is sent to wastewater treatment.

8.10.3.1 Four Bar Steam

The 4 bar steam header is supplied from cyclone A-1902 which is part of the lignin/cellulose drying system shown on PFD 1-351-19. This steam is the water evaporated from the lignin/cellulose being dried.

The 4 bar steam is used in two places. It is first used for preheating the wood feed in bin A-1301 (shown in PFD 1-351-13). Its second process use is at the distillation stripping column A-1803 (shown in PFD 1-351-18). The 4 bar steam supplies all of the heat required for the operation of the distillation columns.

All of the 4 bar steam used during distillation is injected directly and thus is part of the process mixture. This represents the major portion of the 4 bar steam use. This steam becomes part of the liquid bottoms exiting distillation which is subsequently sent to wastewater treatment.

8.10.3.2 One Bar Steam

The 1 bar steam header is supplied from flash tank A-1307 (shown in PFD 1-351-13) at the prehydrolysis step. This header supplies steam to: 1) heat exchanger A-1411 (shown in PFD 1-351-14), where water is heated for washing prehydrolysis residue; 2) the MgO slaking tanks A-1613, A-1614, and A-1615 (shown in PFD 1-351-16) where water is heated to dissolve the MgO; 3) heat exchanger A-1712 shown on PFD 1-351-17 where the feed to fermentation can be heated in cold weather to start the fermentation; and 4) heating coil A-1810 shown on PFD 1-351-18 where the ethanol/water mixture is preheated prior to distillation.

9. PROCESS ECONOMICS

A detailed mass balance/economic model computer program was developed by the SEDF. This interactive software is menu-driven and allows for various process configurations (i.e., virtually any combination of the process areas discussed in Section 8). The mass balance program calculates flow rates, energy contents, etc., for all the streams in each process area. The economic model interacts with the mass balance, and requires such input parameters as local labour rates, local equipment and chemical costs, interest rates, insurance costs, etc. This economic model calculates annual plant capital and production costs based on a chosen write-off period and interest rate (i.e., 10 years and 10%, respectively, used in this analysis). These costs are then related to the ethanol production, and thus, the total annual cost of ethanol produced is arrived at. This calculated ethanol cost, in $/L, is used to gauge the economic feasibility of the process. Given this cost, a variety of other criteria such as "rate of return", can be utilized to take additional considerations (e.g., taxes) into account.

It should be noted that the model requires input cost data in Swedish Krona (SEK) and displays the calculated costs in the same currency unit (NB, exchange rate on July 25/91: $0.1812 (Cdn) = 1 SEK, or $1 (Cdn) = 5.5 SEK). This exchange rate was used to convert the program output into equivalent Canadian dollar values.

Two major process options were considered. Both included the entire CASH process but differed mainly in the requirement for independent utilities (e.g., steam). The first was a "stand-alone" CASH process facility while the other was a CASH plant "coupled" to an existing facility, such as a pulp mill. The mass balances for each of the two options were identical and were calculated according to the "base case" process conditions listed in the next section. The mass balance itself is depicted by way of a flow diagram and an associated spreadsheet in Appendix E.1.

9.1 Base Case Process Conditions

The most probable values for the many process variables, as determined from extensive pilot scale testing, were entered into the mass balance program to develop a "base case". The effect of changing some of these variables on the economics of the process are examined in the sensitivity analysis in Section 9.4. The values of these variables are listed below.

Feed: pine sawdust
100,000 tonne/year (dry basis) @ 40% moisture
composition: 44% cellulose
22% hemicellulose
27% lignin
330 day/year operation

Process Variables: 1st Stage Hydrolysis:
95% of theoretical hemicellulose yield
80% of SO_2 catalyst recovered and recycled
sugar recovery in washing = 92%

2nd Stage Hydrolysis:
glucose/cellulose yield = 50%
cellulose conversion = 65%
sugar recovery in washing = 90-92%

Fermentation:
90% of theoretical ethanol yield

Distillation:
95% ethanol (azeotropic)
22,335 m^3/year produced (may vary slightly according to sugar recovery)

Drying:
lignin/cellulose fuel dried to 85% solids

Wastewater Treatment:
1.20 kg BOD_5/kg organic material in
99% consumption of BOD_5
320 m^3 (NTP) methane produced/tonne BOD_5

Cost Input Data:		
	Feed:	$40/tonne (dry basis)
	Energy:	$3.8/GJ (applies to steam,CH_4, condensate)
	Electricity:	$50/MWh
	Lignin:	$92/tonne (dry basis)

The resultant CASH ethanol plant had a process yield of 224 L ethanol per tonne of dry feed. The detailed mass balance for these "base case" input parameters, which applies to both the "stand-alone" plant and to the "coupled" plant, is shown in Appendix E.

9.2 "Stand-Alone" CASH Facility

This facility includes all of the CASH process areas along with the following peripherals: boiler plants for both high and low pressure steam, plant and instrument air supply, and a wastewater treatment plant. The facility was designed to be completely independent. Though it was suspected that such a facility may not be economically viable, it is included here in order to depict the entire CASH process and for comparison with the "coupled" facility.

Appendix E.1 contains a mass balance, a cost summary, a breakdown of the capital cost according to process area, and an equipment list (including unit prices), for the "stand-alone" CASH facility. Again, note that the costs listed in the program output in the appendix are given in SEK. A conversion factor of 5.5 SEK/$ (Cdn) was used to generate Tables 12 to 14 from the model's output data.

The capital cost summary in Table 12 shows the overall capital cost of the plant to be $83.5 million. Based on a 10 year life for the plant and a 10% interest rate, the annual capital cost is calculated as $14.1 million or $0.633 per litre of 95% ethanol produced. Thus, it appears that the capital cost of a stand-alone facility of this scale may be prohibitive.

As shown in Table 13, the "base case" annual production cost is calculated to be $6.7 million or $0.301 per litre of ethanol. The cost summary in Table 14 shows that the total annual cost of ethanol production for a stand-alone CASH facility of this scale (i.e., 22,335 m³ EtOH/year) would be approximately $0.934 per litre of ethanol.

Table 12. Capital cost summary for "stand-alone" CASH facility (100,000 tonne/year DS feed, 22,335 m^3/year EtOH).

PROCESS AREA	PURCHASE ($1000 (Cdn))	INSTALL'N. & ENG. ($1000 (Cdn))	INSTALLED COST ($1000 (Cdn))
Feed Storage	1,868	1,153	3,021
Prehydrolysis Reactor and Blow Down	2,679	2,677	5,356
Prehydrolysis Wash and Separation	3,218	2,268	5,486
Hydrolysis Reactor and Blow Down	2,341	3,084	5,425
Hydrolysis Wash and Separation	2,472	3,391	5,863
Fermentation	1,287	2,958	4,245
Ethanol Distillation	1,831	2,021	3,852
Lignin Dryer	5,793	2,116	7,909
Briquetting	803	1,086	1,889
Steam Boiler Plant - High Pressure	3,870	3,841	7,710
Steam Boiler Plant - Low Pressure	2,233	3,841	6,074
Wastewater Treatment Plant	3,983	2,235	6,218
Plant and Instrument Air Supply	721	1,882	2,603
Electrical and Instrument Centre	261	903	1,164
SUBTOTAL	33,360	33,456	66,815
Contingency (15%)			10,022
Interest during construction (10%)			6,681
TOTAL			83,518
Capital Cost/Year	10% interest rate	and 10 year write-off	13,592
Working Capital	10% of project	working cap. (5,455)	545
GRAND TOTAL (Capital Cost/Year)			14,137
ANNUAL CAPITAL COST			$0.633/L EtOH

Table 13. Production cost summary for "stand-alone" CASH facility.

PROCESS ITEM	QUANTITY		UNIT PRICE	COST (+) OR CREDIT (-) ($1000 (Cdn))
PRODUCTION COSTS:				
Pine Sawdust	100,000	tonne/year	$40/tonne	4,000
Energy (steam)	640,780	GJ/year	$3.8/GJ	2,447
Power - 60% of	37,738	MWh/year	$50/MWh	1,132
SO_2	445	tonne/year	$260/tonne	116
HCl	523	tonne/year	$240/tonne	125
MgO	552	tonne/year	$309/tonne	171
CaO	959	tonne/year	$196/tonne	188
Nutrients (fermentation)	416	tonne/year	$273/tonne	113
Nutrients (wastewater treat.)	349	tonne/year	$273/tonne	95
Water	1,810,932	tonne/year	$0/tonne	
SUM OF COSTS				8,387
PRODUCTION CREDITS:				
Condensate	188,940	GJ/year	$3.8/GJ	-721
Lignin (dry basis)	32,914	tonne/year	$92/tonne	-3,028
CO_2	14,546	tonne/year	$2.2/tonne	-32
Methane	469,184	GJ/year	$3.8/GJ	-1,791
SUM OF CREDITS				-5,572
PRODUCTION OVERHEAD:				
labour and management				2,364
repair and maintenance				1,364
insurance				182
SUM OF OVERHEAD				3,910
GRAND TOTAL				6,725
ANNUAL PRODUCTION COST				$0.301/L ethanol

Table 14. **Overall cost summary for "stand-alone" CASH plant.**

COST COMPONENT	($1000 (Cdn.))
Production costs	8,387
Production credits	-5,572
Production overhead	3,910
ANNUAL PRODUCTION COST	6,725
ANNUAL CAPITAL COST	14,137
TOTAL ANNUAL COST	20,862
Ethanol production	22,335 m^3/year
ANNUAL ETHANOL COST	$0.934/L EtOH

9.3 CASH Process Plant Coupled to an Existing Facility

This configuration utilizes the entire CASH process but assumes that the plant will be built in close proximity to an existing facility such as a pulp mill/saw mill combination which would serve as a source of feed sawdust. This existing facility would provide steam and air to the CASH process such that these respective process areas would not have to be installed. In addition, it is assumed that the pulp mill's effluent treatment plant is able to process the wastewater generated by the CASH process. Thus, a significant reduction in the capital cost of the process is achieved and one expects the economics to be much more favourable.

The mass balance for the "coupled" plant is identical to that for the "stand-alone" facility and is found in Appendix E.1. The cost summary output from the economic model program is shown in Appendix E.2. Printouts of the process area summary and the equipment summary were not included for the "coupled" case because the same information can be obtained from the corresponding printouts for the "stand-alone" plant in Appendix E.1.

Table 15 shows the capital cost summary for the coupled CASH plant. The overall capital cost, at $55.2 million, is approximately two-thirds that of the stand-alone facility. The annual capital cost is calculated to be $9.4 million or $0.419 per litre of ethanol produced. The production cost for the coupled facility, operating with the "base case" process conditions, are itemized in Table 16. The annual production cost is determined to be 5.2 million dollars or $0.234 per litre of ethanol. The overall cost summary in Table 17 shows that the total cost of ethanol production for such a coupled facility, given the "base case" operating parameters would be $0.653 per litre of ethanol.

Table 15. Capital cost summary for "coupled" CASH facility (100,000 tonne/year DWS feed, 22,335 m^3/year EtOH).

PROCESS AREA	PURCHASE ($1000 (Cdn))	INSTALL'N. & ENG. ($1000 (Cdn))	INSTALLED COST ($1000 (Cdn))
Feed Storage	1,868	1,153	3,021
Prehydrolysis Reactor and Blow Down	2,679	2,677	5,356
Prehydrolysis Wash and Separation	3,218	2,268	5,486
Hydrolysis Reactor and Blow Down	2,341	3,084	5,425
Hydrolysis Wash and Separation	2,472	3,391	5,863
Fermentation	1,287	2,958	4,245
Ethanol Distillation	1,831	2,021	3,852
Lignin Dryer	5,793	2,116	7,909
Briquetting	803	1,086	1,889
Electrical and Instrument Centre	261	903	1,164
SUBTOTAL	22,553	21,657	44,210
Contingency (15%)			6,632
Interest during construction (10%)			4,421
TOTAL			55,263
Capital Cost/Year	10% interest rate	and 10 year write-off	8,994
Working Capital	10% of project	working cap. (3,636)	364
GRAND TOTAL (Capital Cost/Year)			9,358
ANNUAL CAPITAL COST			$0.419/L EtOH

Table 16. . Production cost summary for "coupled" CASH facility.

PROCESS ITEM	QUANTITY		UNIT PRICE	COST (+) OR CREDIT (-) ($1000 (Cdn))
PRODUCTION COSTS:				
Pine Sawdust	100,000	tonne/year	$40/tonne	4,000
Energy (steam)	640,780	GJ/year	$3.8/GJ	2,447
Power - 60% of	28,409	MWh/year	$50/MWh	852
SO_2	445	tonne/year	$260/tonne	116
HCl	523	tonne/year	$240/tonne	125
MgO	552	tonne/year	$309/tonne	171
CaO	959	tonne/year	$196/tonne	188
Nutrients (fermentation)	416	tonne/year	$273/tonne	113
Nutrients (wastewater treat.)	349	tonne/year	$273/tonne	95
Water	1,810,932	tonne/year	$0/tonne	
SUM OF COSTS				8,107
PRODUCTION CREDITS:				
Condensate	188,940	GJ/year	$3.8/GJ	-721
Lignin (dry basis)	32,914	tonne/year	$92/tonne	-3,028
CO_2	14,546	tonne/year	$2.2/tonne	-32
Methane	469,184	GJ/year	$3.8/GJ	-1,791
SUM OF CREDITS				-5,572
PRODUCTION OVERHEAD:				
labour and management				1,455
repair and maintenance				1,091
insurance				136
SUM OF OVERHEAD				2,682
GRAND TOTAL				5,217
ANNUAL PRODUCTION COST				$0.234/L ethanol

Table 17. **Overall cost summary for "coupled" CASH plant.**

COST COMPONENT	($1000 (Cdn.))
Production costs	8,107
Production credits	-5,572
Production overhead	2,682
ANNUAL PRODUCTION COST	5,217
ANNUAL CAPITAL COST	9,358
TOTAL ANNUAL COST	14,575
Ethanol production	22,335 m^3/year
ANNUAL ETHANOL COST	$0.653/L EtOH

9.4 Sensitivity Analysis

The effect of changing the process and cost input data, on total annual cost of ethanol production (i.e., in $/L of EtOH), was examined using the "coupled" CASH facility case. In each case, the parameters other than the one being studied have the "base case" value, as outlined in section 9.1.

9.4.1 Feedstock Cost

The cost of the pine sawdust feedstock in the "base case" was $40/tonne (dry basis). This is somewhat less than the value of the material as a fuel to account for the fact that it is, at present, a waste stream with an associated disposal cost (i.e., assuming wood has a fuel value of 19 GJ/tonne and energy = $3.8/GJ, cost should be approximately $72/tonne). If the waste disposal problem becomes very significant, there is the potential for zero or negative feedstock costs.

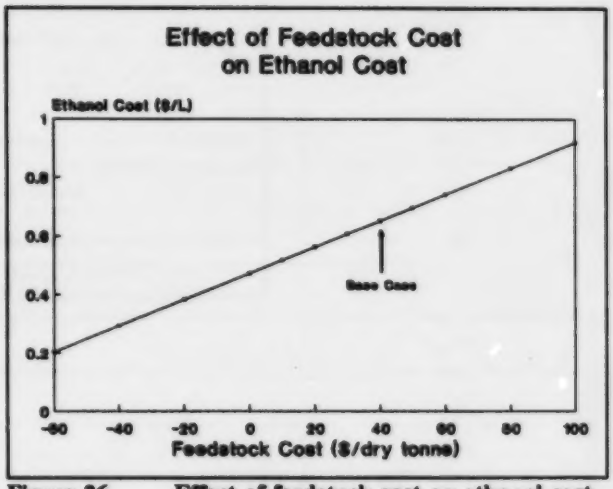


Figure 26. Effect of feedstock cost on ethanol cost.

Figure 26 shows a plot of ethanol cost vs. feedstock cost for a coupled CASH facility. The data itself is contained in Table E.1 in Appendix E.3. Since the capital cost of the plant remains unchanged at $0.418/L, this sensitivity plot reflects the change in production cost resulting from varying the cost of the feed material. The base case production cost was $0.233/L and thus, the total ethanol cost was $0.65/L. The graph shows that the ethanol costs range from $0.20/L up to $0.92/L as the feedstock cost is increased from $-60/tonne to $100/tonne. For a zero cost feedstock, the cost of ethanol becomes $0.47/L. It is possible for the feedstock cost to be negative, if one considers waste disposal expenses such as tipping fees. With negative feedstock costs, the production cost actually becomes negative. For example, with the feed at $-20/tonne, the production cost is $-0.035/L, and thus, the total ethanol cost becomes $0.383/L.

This analysis shows that the ethanol cost is a very strong function of feedstock cost. Its importance can be confirmed by noting that the feedstock represents the single largest component of the production cost in Table 16. Therefore, obtaining an inexpensive feed is perhaps the most important external factor (i.e., independent of process considerations) in attaining economic viability.

9.4.2 Lignin Credit

The base case selling price for the dried lignin/cellulose hydrolysis residue was based solely on its fuel value (i.e., assume 24.4 GJ/tonne @ $3.8/GJ or $92/tonne). If it became possible to use the lignin as a chemical reagent, or the price of energy rose, one could foresee a higher price for this CASH process co-product. Figure 27 shows the effect of the lignin credit on the overall cost of ethanol produced by a coupled CASH plant. The data, from which the graph was generated, is listed in Table E.2 of Appendix E.3.

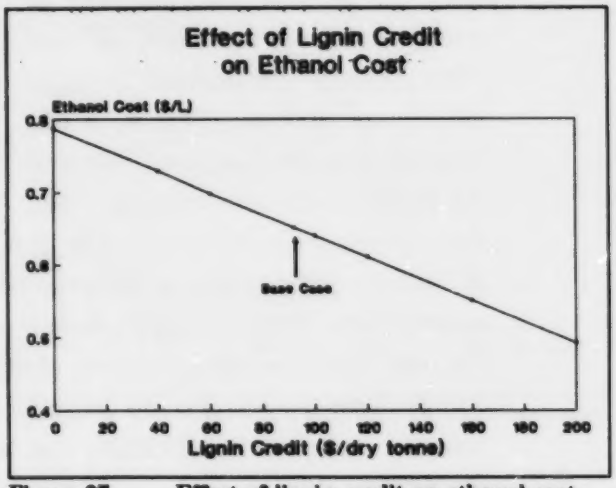


Figure 27. **Effect of lignin credit on ethanol cost.**

The lignin/cellulose fuel is the most significant contributor to the production credits (see Table 16). Therefore, it is no surprise that the production cost of ethanol, and hence the overall cost, is a strong function of the lignin price. The figure shows that if the lignin somehow retained its reactivity, and it could be sold as a chemical precursor at $200/tonne, the total cost of ethanol produced would be $0.493/L (representing a production cost of only $0.075/L).

9.4.3 Price of Energy

The price of energy included in the base case was \$3.8/GJ and was calculated on an assumed oil price of \$21(US)/barrel. In determining the effect of the energy price, three possible circumstances were examined.

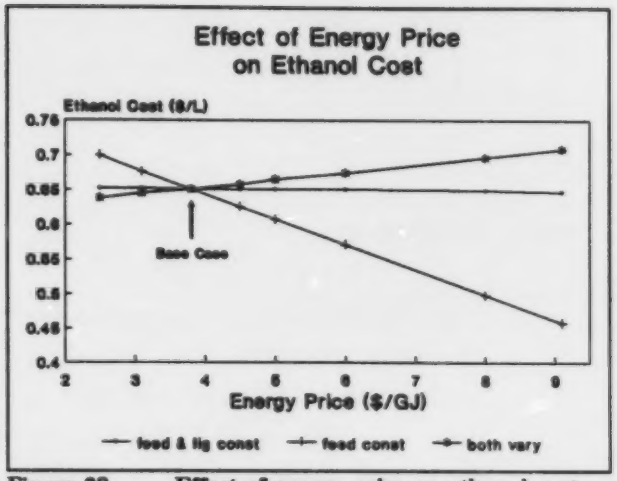


Figure 28. Effect of energy price on ethanol cost.

In the first case, the price of energy itself, independent of any other process components it might affect, was studied. That is, it was assumed that the feedstock cost and the lignin credit were constant. The data for this graph is contained in Table E.3 in Appendix E.3. It is evident from Figure 28 that the price of energy itself has no effect on the price of ethanol. This reflects the balance between the "energy" streams of the process. It can be seen from Table 16 that the quantity of steam consumed (640,780 GJ/year) is almost equal to the quantity of energy in the condensate and methane streams (658,124 GJ/year). Therefore, even if the assumed energy price (\$3.8/GJ) was incorrect, it would not affect the overall process economics.

The second case assumed that the cost of the feed was constant while the price of the lignin fuel varied in direct proportion to the energy price. Such a circumstance would be possible if the feed represented an unused waste stream which had no practical value as a fuel, while the lignin represented a desirable solid fuel. The data for this case is found in Table E.4 in Appendix E.3 and is depicted in Figure 28. The ethanol cost is seen to drop with the increasing energy price in much the same way as it did with increasing lignin credit (Figure 27).

In the third case, both the feed cost and the lignin price vary according to the price of energy. The raw data, which is plotted in Figure 28, appears in Table E.5 of Appendix E.3. The cost of ethanol increases slightly with increasing energy price. For example, the cost of ethanol with the base case energy price of \$3.8/GJ is \$0.65/L, while with an energy

price of $8/GJ, the ethanol cost becomes $0.70/L. In comparing this third case with the second, it becomes apparent that the feed cost has more of an effect on the process economics than the lignin credit (also noticeable in Table 16).

9.4.4 Price of Electricity

The effect of the price of electricity on process economics is shown in Figure 29 (data in Table E.6, Appendix E.3). The ethanol cost is not a very strong function of the cost of electricity but it does nevertheless increase. It is interesting to note that if the existing facility, to which the CASH plant is coupled, has a generator (e.g., some pulp mills), the cost of the ethanol produced would drop to $0.61/L from the base level of $0.65/L.

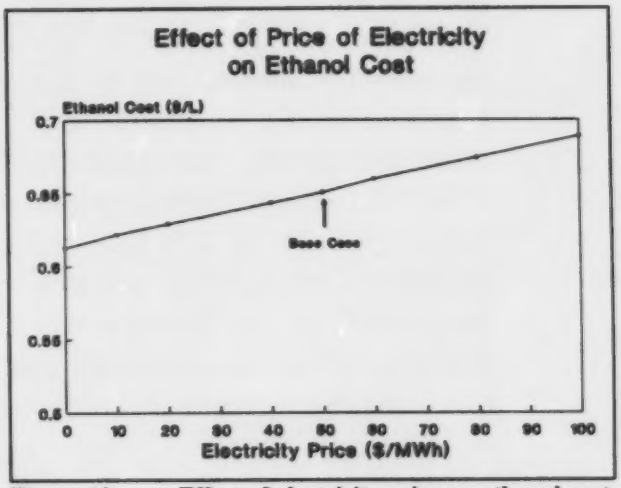


Figure 29. Effect of electricity price on ethanol cost.

9.4.5 Hydrolysis Yield

Hydrolysis yield (i.e., glucose/initial cellulose), being a key process parameter, may affect the capital cost of the plant as well as the production cost. Thus, two cases were studied depending upon the design basis for the plant. In the first case, the plant was designed to produce approximately 22,400 m^3/year of 95% ethanol. If the hydrolysis yield of the process decreased, there had to be a corresponding increase in the amount of sawdust that was fed to the process in order to maintain the level of ethanol production. Thus, the overall capital cost changed according to the scale of the plant. The second case utilized a constant feed rate and allowed the ethanol production to change according to the changing hydrolysis yield. In this case, the overall capital cost remained constant while the production cost varied according to the quantity of ethanol produced. The two cases

are depicted in Figure 30 and the respective data is contained in Tables E.7 and E.8 in Appendix E.3.

Both cases show that the ethanol cost drops as the hydrolysis yield increases. In the first case, the volumetric ethanol output of the plant is constant regardless of the hydrolysis yield. Thus, the per litre cost shown is affected only by cost considerations and not differences in production volumes. The capital cost of the plant increases as the hydrolysis yield drops below the 50% base case (capital cost increases by a scaling factor raised to the exponent 0.7). Strangely enough, the production costs decrease marginally as the yield falls (because of increased lignin and methane credits). The overall effect is that, for the case of constant ethanol output, the price of ethanol increases slightly with decreasing yield.

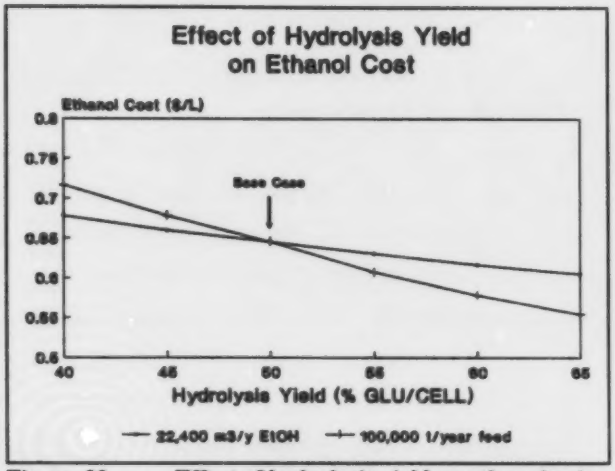


Figure 30. Effect of hydrolysis yield on ethanol price.

In the case of constant feed rate (i.e., 100,000 tonne/year designed capacity), the overall capital cost (but not the capital cost per unit ethanol) of the plant remains the same while the production cost varies. The ethanol cost is more sensitive to hydrolysis yield in this case because there is a direct relationship between the quantity of ethanol produced and its unit capital and production costs (as compared to the change in capital cost in the first case which only varied according to the scaling factor raised to the power of 0.7). Assuming that a 60% yield could be achieved without adversely affecting the fermentability of the hydrolysate, the total cost of ethanol produced would drop to $0.58/L from $0.65/L in the base case.

9.4.6 Fermentation Yield

The cases under which the effect of fermentation yield was tested were much the same as those above for hydrolysis yield. The results shown in Figure 31 are quite similar as well. The raw data for the two cases are in Tables E.9 and E.10 in Appendix E.3. The constant feed rate case proved to be more sensitive to fermentation yield than did the constant ethanol production case.

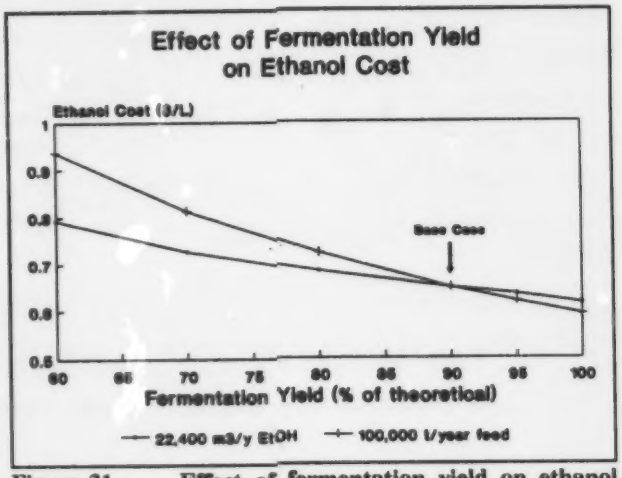


Figure 31. Effect of fermentation yield on ethanol cost.

9.4.7 Hydrolysis Separation Equipment

The process includes a single decanter/centrifuge for each of the counter-current washing steps after second stage hydrolysis. However, given the nature of the material to be separated and the results of the pilot scale runs, three machines in parallel may be required for each of the washing steps. This matter is, as yet, unresolved but depends on the existence of machines which can handle the high volumetric throughput required and still provide the necessary residence time for adequate separation.

If three such machines were required at each washing step, the base case annual capital cost would increase to $0.451/L (from $0.418/L) and the annual production cost would rise fractionally to $0.244/L (from $0.234/L). The resultant total annual cost of ethanol production would increase to $0.695/L from $0.653/L.

9.4.8 Best Achievable Process Parameters

The process parameter values entered into the base case were the most reasonably achievable levels. It is interesting to note the effect on the ethanol cost of inserting the best possible outcomes for the variables that are within the control of the process itself. The following values were entered into the process:

Sugar recovery (both stages):	95%
Hydrolysis yield:	60% glucose/cellulose
Fermentation yield:	95% of theoretical

Table 18 shows the result of making these "best case" assumptions and includes the effect of feedstock cost and lignin credit (even though these are not "process variables").

Table 18. Effect of "best case" process variables

Feed Cost ($/dry tonne)	Lignin Cost ($/dry tonne)	Ethanol Prod. (m^3/year)	Ethanol Yield (L/tonne)	Annual Capital Cost ($/L)	Annual Production Cost ($/L)	Total Annual Cost ($/L)
40	92	27,479	275	0.340	0.202	0.542
0	92	27,479	275	0.340	0.056	0.396
0	120	27,479	275	0.340	0.029	0.369

The process ethanol yield under these conditions was increased to 275 L/tonne (from approximately 224 L/tonne in the base case) and this had a significant effect on the unit production and capital costs. The capital cost fell from $0.418/L to $0.340/L while the production costs fell from $0.234/L to $0.202/L. Thus, with the best case process variables, the overall cost of ethanol produced fell quite significantly from $0.653/L to $0.542/L. If these best case process variables are combined with a zero feedstock cost, the cost of ethanol produced becomes $0.396/L. If these conditions are combined with both a zero feedstock and an increased lignin credit, the cost of ethanol produced falls further to $0.369/L. Therefore, it is seen that there is a significant return for achieving the optimum process conditions.

9.4.9 Scale of the CASH Facility

Because of the dominant effect of the plant capital cost on process economics, it is suspected that increasing the scale of the plant could only improve the ethanol cost. A "base case" plant with twice the capacity (i.e., 200,000 tonne DS/year feed) was found to produce 45,218 m^3/year EtOH with a capital cost of $0.33/L and a production cost of $0.15/L. The resultant improvement in the total annual cost of ethanol produced (i.e., $0.48/L vs. $0.65/L) suggests that operating a larger scale facility may be essential.

If the best achievable process parameters and a zero feedstock cost are inserted into the model for the large-scale facility, the resulant plant would produce 55,200 m^3/year EtOH with an overall cost of $0.28/L.

10. CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

The optimum operating conditions for the SO_2-catalyzed prehydrolysis of pine chips using TVA's Sunds Defibrator were a temperature of 160°C, a residence time of 30 minutes, an SO_2/wood (dry basis) ratio of 2.5%, and a water/dry solid ratio of 3/1 in the reactor. Such conditions produced yields of hemicellulose sugars which exceeded 90% of the theoretical.

In second stage hydrolysis, cellulose-to-glucose conversions of over 50% were attainable but the fermentability of the resultant hydrolysate was of overriding importance in selecting the best operating conditions for the plug flow reactor.

Temperature, acid concentration, and residence time were the plug flow reactor (PFR) variables examined. Through a statistical experimental design, it was found that with one of these three variables at its "high" level, cellulose-to-glucose conversions exceeding 40% could be achieved and the resultant hydrolysates were fermentable. When two of the three reaction variables were at their "high" level, higher cellulose-to-glucose conversions were obtained (~50%), but higher levels of glucose degradation products (which acted as fermentation inhibitors) were produced, and as a result the hydrolysates were virtually unfermentable. With each of the three reaction variables at their respective "high" levels, low cellulose-to-glucose conversions were detected (suggesting that the peak glucose conversion had been passed) and the hydrolysates themselves were not fermentable.

Conditions of high temperature (225-230°C), short residence time (0.5-0.7 min), and low acid concentration (0.2-0.25% HCl in solution) were chosen to be optimal from the standpoint of both glucose yield and hydrolysate fermentability.

Some hydrolysates produced under these "optimal" conditions proved to be fermentable at concentrations of 12-14% sugar. Repeated runs at the "optimal" PFR conditions produced cellulose-to-glucose conversions which were typically 40-45% and most of the hydrolysates were fermentable at concentrations of 6-8% sugar. It appeared that a measured cellulose-to-degradation products conversion of 10-12% was somewhat of a threshold in achieving a fermentable hydrolysate.

A theoretical kinetic model for the weak acid hydrolysis of cellulose predicted the experimental maxima in cellulose-to-glucose conversion quite well. However, the measured conversions were not as sensitive to the reaction conditions (especially residence time and acid concentration) as the model predicted.

The separation of the soluble stream (sugar solution) from the lignin/cellulose residue of second stage hydrolysis was carried out using a scroll decanter/centrifuge. Sugar recovery in the decantate was found to improve with increasing feed rate, and decrease with increasing feed solids content. It was not significantly affected by feed temperature while the flocculent Berocell had a detrimental effect. Recovery of suspended solids in the underflow of the decanter was found to decrease with feed solids content and with feed flow. Higher feed temperatures improved the recovery of suspended solids while Berocell had no significant effect.

The residue of second stage hydrolysis, for runs with cellulose-to-glucose conversions of ~50%, was found to consist of 17-21% unreacted cellulose and 78-82% lignin. Pilot-scale dryer tests in Sweden proved that the second stage residue, which exited the centrifuge/decanter at ~25% dry solids, was relatively simple to process. The product was dried to over 95% dry solids and left no deposits in the dryer unit. The water, which is evaporated from the residue in this process area of the CASH plant, will eventually be sent to the waste water treatment facility. It was encouraging to find that the chemical oxygen demand (COD) of this water stream was quite low. A particle-size analysis of the dried residue showed that 80% of the particles were smaller than 500 microns.

Based on its resistance to wood-derived inhibitors and its ability to grow on both hemicellulose and cellulose hydrolysates, a strain of *Saccharomyces cerevisiae* was selected as the process organism. This strain was acclimatized to cellulose hydrolysates and became known as the CASH1 strain.

Various hydrolysate clean-up procedures were tested relative to their ability to render the wood hydrolysates less inhibitory to the process organism (CASH1). A treatment which consisted of elevating the pH of the hydrolysate to 10-10.5 with CaO, followed by the addition of sodium sulphite (1 g/L) and heating for 30 minutes (at 90°C), was found to appreciably improve the fermentability of the hemicellulose hydrolysate. This treatment was used for all of the batch fermentation trials. The cellulose hydrolysate was neutralized

with MgO (because Mg salts were found to be less inhibitory than those produced from other neutralizing agents) but was not treated in any other way.

Small-scale (1L) batch fermentations were carried out using 50/50 mixtures of hemicellulose and cellulose hydrolysates. Synthetic mixtures of pure sugars, which corresponded to the levels occurring in the hydrolysate mixture, were used for control fermentations. Although the hydrolysate mixtures had slightly lower rates of sugar utilization and ethanol production than the controls, it appeared that the inhibitory effects of the wood hydrolysates were manifested primarily during cell growth. The ethanol yields were typically 92% of the theoretical (i.e., 0.46-0.47 g EtOH/ g fermentable sugar) for both the hydrolysate mixture and the control.

Pilot-scale (100L) fermentations of a 50/50 mix of hemicellulose and cellulose hydrolysates showed sugar utilization rates, ethanol production rates, and cell growth rates which corresponded to those in the lab fermentations. Ethanol yields were lower but this was largely due to evaporative loss of ethanol during the course of the fermentation. Each of the pilot runs were complete within approximately 30 hours. These pilot runs were carried out with initial sugar concentrations of approximately 50 g/L.

A mass balance and economic analysis was carried out using a program developed by the Swedish Ethanol Development Foundation (SEDF). Using "base case" process conditions, the process ethanol yield for the CASH plant would be approximately 224 L of 95% ethanol per tonne of dry pine sawdust feed. Given the base case process assumptions and a 100,000 tonne/year (dry basis) pine sawdust feed rate, a "stand-alone" facility can produce ethanol for an annual cost of $0.93 per litre. Such a facility would not be feasible based on economic considerations alone.

If the CASH process plant is integrated or "coupled" with an existing facility, the total annual ethanol cost for the base case conditions would be $0.65/L. Of this, $0.42/L represents the annual capital cost. This predominance of the capital cost suggests that the scale of the facility should have a significant effect on its economic feasibility. Indeed, if the scale is doubled (i.e., 200,000 tonne/year DWS feed or 45,000 m^3/year ethanol), the total annual cost of the ethanol produced drops to $0.48/L for the base case.

Sensitivity analyses on the "coupled" facility show that the annual production cost is a very strong function of feedstock cost. In the base case, this was assumed to be $40/dry tonne. If the feedstock cost was zero, the total annual ethanol cost would be $0.47/L. For a negative $20/tonne feedstock cost, the ethanol cost becomes $0.38/L. The credit for the co-product lignin fuel was also found to have a significant effect.

Because the energy consumption streams (i.e., process steam) are well balanced with the energy production streams (i.e., methane from the waste water treatment facility and steam condensate), the price of energy does not have a significant effect on the ethanol production cost. Both the hydrolysis yield and the fermentation yield affect the annual cost of ethanol quite significantly, suggesting that process optimization is critical. In the event that the best achievable process parameters were attained in the production facility, the ethanol cost drops to $0.54/L (all other assumptions the same as the base case). If these optimal process conditions were coupled with a zero feedstock cost, the cost of the ethanol produced falls to $0.40/L.

10.2 Recommendations

Other potential feedstocks should be studied in more detail to provide an indication of how process conditions and yields will differ.

A semi-industrial-scale demonstration facility should be developed.

Hydrolysate clean-up methods such as solvent extraction and steam stripping should be studied in more detail.

Pilot-scale fermentations should be performed at higher hydrolysate sugar concentrations (i.e., 6-8%). In addition, the continuous cascade fermentation system that is included in the process design should be tested at a pilot scale.

Pentose-fermenting organisms should be studied using the hydrolysates generated in this project.

A comprehensive investigation of potential uses and markets for industrial- and fuel-grade ethanol should be carried out.

The suitability of utilizing un-dried lignin/cellulose residue as a boiler fuel should be determined. A significant capital cost savings could be achieved if the lignin dryer section was not included in the CASH process facility.

Because of the potentially very high capital cost of several scroll decanters, alternative schemes for the separation of the hydrolysis residue from the soluble stream should be examined. Perhaps other flocculents could be tested.

REFERENCES

Braconnot, H. 1819. Hydrolysis of Cellulose into Sugar. Gilbert's Annalen der Physik. 63:348.

Braun, W. 1965. *In* Bacterial Genetics. L.B. Saunders (ed). p. 20.

Bungay, H.R. 1982. Biomass Refining. Science 218(4573):643.

Cederquist, K.N.. 1954. "Some Remarks on Wood Hydrolyzation in the Production and Use of Power and Alcohol in Asia and the Far East." Report of Seminar (October 23--November 6, 1952. Lucknow, India) New York: United Nations:193-197.

Chen, C.C., and McGinnis, G.D. 1981. The use of 1-methylimidazole as a solvent and catalyst for the preparation of aldononitrile acetates of aldoses. Carbohydrate Research 90(1):127-130.

Faber, M.D., R.H. Ernst, and P.H. Lefebvre. 1982. Fermentaable acid hydrolyzates and fermentation processes. U.S. Patent No. 4,342,831.

Grethlein, A.E., and A.O. Converse. 1982. Continuous acid hydrolysis for glucose and xylose production. *In* Duckworth, H.E., and E.A. Thompson (eds). Intl Symp on Ethanol from Biomass. Royal Society of Canada, Ottawa. pp. 312-333.

Gilbert, N. 1952. Hydrolysis of Wood Using Dilute Sulfuric Acid. Industrial and Engineering Chemistry 44:1712.

Kuster, B.F.M. 1990. 5-Hydroxymethylfurfural (HMF). A review focussing on its manufacture. Starch 42(8):314-321.

Leonard, R. H., and G.J. Hajny. 1945. Fermentation of wood sugars to ethyl alcohol. Ind. Eng. Chem. 37:390-395.

Locke, E.E.G. 1945. The Production of Wood Sugar in Germany and Its Conversion to Yeast and Alcohol. Field Information Agency, Technical Joint Intelligence Objectives Agency, Washington, D.C.

Perry, R.H., D.W. Green, and J.O. Maloney. (eds.). 1984. Perry's Chemical Engineer's Handbook. 6th ed. McGraw-Hill, Toronto.

Rydholm, S.A. 1965. Pulping Processes. Garden City Press, Ltd., Letchworth, Hertfordshire, England. p. 823.

Saemen, J.F. 1982. Acid Hydrolysis of Cellulosics (A "Panoramic" View). Royal Society of Canada, International Symposium on Ethanol from Biomass. Ottawa, Canada.

Shreve, R.N. 1956. The Chemical Process Industries. Second Edition. McGraw-Hill Book Co., Inc. p. 717.

Simonsen, E. 1898. Zeit. fur angw. Chmie.:195-962, 1007.

Stowe, R.A., and R.P. Mayer. 1966. Efficient screening of process variables. Ind. Eng. Chem. 58:36-40.

Walpole, R.E., and R.H. Meyers. 1978. Probability and Statistics for Engineers and Scientists, 2nd edition. Macmillan Pub. Co., Inc. N.Y.

Wayman, M., J.H. Lora, and E. Gulbinas. 1979. Material and energy balances in the production of ethanol from wood. *In* Tomlinson, M. (ed.). Chemistry for Energy, ACS Symposium Series. ACS, Washington, D.C. pp. 183-201.

Westmoreland, R.A., R.L. Griffith, S. Wannstrom, and J. Kolar. 1988. Production of ethanol by dilute acid hydrolysis of Swedish feedstocks. *In* New Energy and Industrial Technology Development Organization (ed.). Proc. VIII Intl. Symp. on Alcohol Fuels. Sanbi Insatsu Co., Ltd. pp. 55-60.

APPENDICES

APPENDIX A

ANALYTICAL METHODS

A.1 Dry and Suspended Solids

The total dry solids of the various samples (e.g., hydrolysis products, decanter streams, etc.) were measured by weighing uniform, well-mixed portions into tared crucibles. The crucibles were dried in a lab convection oven (Blue-M Stabiltherm) for at least 16 hours at 100-106°C. The crucibles were cooled in a sealed desiccator and weighed. The percent dry solids (DS) was calculated as:

$$\%DS = \frac{\text{wt of dried sample}}{\text{wt of original sample}} \times 100\%$$

The suspended solids (undissolved) were determined by taking a known weight of sample (60-120 g, as measured on an analytical balance), diluting it with warm water, and performing a vacuum filtration through a pre-weighed Whatman GF/A filter. The cake was washed thoroughly with warm water (500-1000 mL) to ensure the removal of all soluble solids. The cake and filter were dried for at least 16 hours at 100-106°C in a lab convection oven, cooled in a desiccator, and weighed. The % suspended solids was calculated by dividing the dried weight of the undissolved solids by the original sample weight. Note that for some analyses, the soluble portion from the vacuum filtration was collected, quantified and analyzed for its sugar composition. This was one alternate method of estimating the conversion of the feed to sugars.

A.2 Sugar Analysis

The sugar content of various aqueous streams (eg., hydrolysates) was primarily determined using High Pressure Liquid Chromatography (HPLC).

For cellulose hydrolysis products from the plug flow reactor, a uniform, representative sample of product (30-40 g) was neutralized with 50% NaOH (5-10 drops), centrifuged and decanted. The aqueous portion was filtered through a 0.45 micron filter and injected into the HPLC.

The HPLC unit consisted of a Beckman 110B Solvent Delivery Module, a Valco UHP-7K automatic injector, a Waters R-401 Differential Refractometer Detector, and a Shimadzu C-R3A Chromatopac Integrator. One of two columns was used to analyze the component sugars of these hydrolysates. The organic-acid/sugar column was a Bio-Rad HPX 87H (column temperature = 40°C, mobile phase = 0.01 N H_2SO_4, flow rate = 0.6 mL/minute). It had the disadvantage of co-elution of galactose, mannose and xylose. The carbohydrate column which allowed the separation of these peaks was a Bio-Rad HPX 87P (column temperature = 60°C, mobile phase = distilled de-ionized water, flow rate = 0.6 mL/minute).

The integrator was programmed, for each column, using an external standard, absolute calibration curve method. The 87H column was used primarily for the analysis of cellulose hydrolysates with the major components being glucose (retention time=9.2 minutes), levulinic acid (16.5 minutes), and 5-hydroxymethyl furfural (34 minutes). The 87P column was ideal for hemicellulose hydrolysates because all of the sugars were separable (i.e., glucose, 12.3 minutes; xylose, 13.6 minutes; galactose, 14.6 minutes; arabinose, 16.3 minutes; mannose, 17.6 minutes).

Rapid glucose determinations (with concentrations as low as 0.5 g/L) were performed using the YSI (model 27) Glucose Analyzer. When very precise and accurate measurements were needed, the sugars were determined using the aldol acetate derivitization procedure and capillary gas chromatography (Chen and McGinnis, 1981). The sugar concentrations during the fermentations were monitored via this method.

A.3 Ethanol Analysis

Ethanol concentrations in fermentation samples were measured either by HPLC with the HPX 87H column (ethanol retention time, 21.7 minutes) or using an enzymatic method (Boehringer Mannheim Kit No. 176290).

A.4 Acid Insoluble (Klason) Lignin, Hemicellulose and Cellulose

Acid insoluble (Klason) lignin, in solid samples, was determined using a method which allowed the simultaneous quantification of cellulose and hemicellulose.

Fifteen mL of 72% H_2SO_4 was added to one gram of finely ground (< 28 mesh) dried material. This mixture was digested at 20°C for 2 hours with occasional stirring. It was then transferred quantitatively to a 500 mL flask and diluted to 415 mL. The flask was autoclaved for 2 hours at 15 psig (121°C) to complete the hydrolysis and produce a solution of sugar monomers. The solution was cooled and its volume (weight) was re-adjusted to 415 mL. The solution was filtered through a weighed Whatman GF/A filter paper and the collected residue was dried. This residue was classified as acid-insoluble lignin (Klason). The filtrate was neutralized and de-ashed using powdered $CaCO_3$. Filtering removed the $CaSO_4$ which was formed and left a solution free of ash. This final filtrate (normally with a volume of 410-430 mL) was analyzed for sugar monomers by HPLC (NB, YSI glucose analyzer was sometimes used if the material contained no hemicellulose).

The cellulose and hemicellulose contents of the known weight of original material were calculated using the concentrations determined by HPLC, the appropriate solution volumes and knowing the chemical gain associated with the hydrolysis of hexose polymers (11.1%) and pentose polymers (13.6%).

A.5 Calculation of Glucose Yield (or Cellulose Conversion to Glucose) in Second Stage Hydrolysis

i) Original method

This calculation was based on the determination of the glucose concentration in the aqueous fraction of the hydrolysis product, and on measuring the water volume associated with this glucose concentration (i.e., calculated from the product dry solids level as determined by oven drying). The product solids were assumed to consist of glucose, residual cellulose and "others" (i.e., lignin and any component other than cellulose in the

original feed material were assumed not to react). Using these assumptions, an expression for the glucose/cellulose yield was developed as follows.

BASIS:
100 g wet feed

MEASURED VARIABLES:
DSF - % dry solids in the feed
DSP - % dry solids in the product
x_c - weight fraction cellulose in dry feed (approx. 0.5 for TVA residue)
C_g - concentration of glucose in product supernatant (g/L)

UNKNOWN VARIABLE:
f_g - fractional yield of glucose from the feed cellulose

CALCULATED VARIABLES:
$m_c = x_c*DSF$ (wt. cellulose in feed (g))
$m_g = f_g*m_c$ (wt. GLU produced from feed cellulose (g))
$m_{cr} = (1-(f_g/1.111))*m_c$ (residual cellulose in product (g))
$m_{oth} = (1-x_c)*DSF$ (lignin & others constituents of both feed and product)
$TS = m_g+m_{cr}+m_{oth}$ (total solids in product (g))
$V_w = TS*Q$ where $Q=(100-DSP)/DSP$ (volume of water in product (mL) assuming density=1 g/mL)
$m'_g = C_g*V_w/1000$ (wt. glucose in product sample (g))

CALCULATION:
Solve for $f_g = m'_g/m_c$

$f_g=C_g*V_w/(1000*m_c) = (C_g*TS*Q)/(1000*x_c*DSF)$

after some manipulation, this equation reduces to:

$f_g = (C_g*Q)/[x_c*(1000-0.10*C_g*Q)]$ where $Q=(100-DSP)/DSP$

Thus, the equation represents the glucose produced divided by the initial cellulose (i.e., the fractional yield of glucose from cellulose).

The following assumptions were made: 1) Only glucose, residual cellulose and lignin exist in the product; it does not account for the degradation of glucose to HMF, levulinic acid, etc.; as a result, the expression representing the initial cellulose (denominator of above equation) is slightly low and the glucose yield calculated is high. 2) Determination of the volume of water in the product using the DSP value can produce false high results (for water volume) if the measured DSP is lower than it should be based on the DSF and theoretical flash calculations; i.e., this would occur if volatiles were produced and were not detected as solids in the oven-drying method (or were flashed off with the steam at the discharge of the reactor).

ii) More rigorous method to account for glucose degradation products

In order to determine the volume of water associated with C_g in the supernatant, the above calculation made the simplifying assumption that cellulose only reacted to form glucose. However, this certainly is not the case and thus, glucose degradation products should be included in the calculation. For this calculation, it was assumed that the original cellulose either reacted to form glucose, HMF, and levulinic acid (and formic acid in equimolar quantities), or was left as unreacted cellulose. Other cellulose reaction products may exist but these were not considered here.

	MOLECULAR WEIGHTS:	RATIO OF MOLECULAR WEIGHTS:
cellulose	162	
glucose	180	$M_{cell}/M_{glu}=0.90$
HMF	126	$M_{cell}/M_{HMF}=1.286$
levulinic acid	116	$M_{cell}/M_{lev}=1.397$
formic acid	46	$M_{cell}/M_{for}=3.522$

Terms for HMF, levulinic acid and formic acid and their respective weight losses relative to the initial cellulose, were included in the expression for total solids in the product (TS). The overall expression for glucose yield from initial cellulose became:

$$f_g = C_g*Q/\{x_c*[1000-C_g*Q*(0.10-0.286*C_{HMF}/C_g-0.397*C_{lev}/C_g-2.522*C_{for}/C_g]\}$$

This rigorous approach used the measured concentrations of HMF, levulinic acid and formic acid to calculate the initial amount of cellulose in the feed. Thus, by making adjustments for the chemical weight loss when products other than glucose were formed, the initial quantity of cellulose (the denominator of the above expression; as calculated on a product basis) was effectively increased over the situation when it was assumed that only glucose was produced. Alternatively, one can look at the adjustment as having decreased the total solid (TS) term and hence, the volume of water (V_w) associated with the glucose concentration in the decantate (C_g). Accordingly, this rigorous method resulted in lower calculated glucose yields (particularly for runs in which significant glucose degradation took place).

iii) Calculation using a theoretical flash factor

One can calculate the amount of water that should be present in the reactor product given the reaction temperature and the fact that the product was discharged to atmospheric pressure. A theoretical "flash factor" (or percent of water in the feed which flashed at the reactor discharge) was calculated by performing an energy balance.

If the theoretical flash factor was used, the applicable equations becomes:

W_{feed} = 100-DSF (water in the feed (g or mL))
$W_{prod} = W_{feed}$ - (%flash)*W_{feed} (water in the product (g or mL))
$m_g = C_g * W_{prod}/1000$ (wt. glucose in product (g))
$m_c = x_c * DSF$ (wt. cellulose in feed (g))

Thus, the fractional glucose yield based on initial cellulose was:

$f_g = m_g/m_c$

It was found that for most runs, the yield calculated using this theoretical flash procedure agreed quite well with the yields calculated using the "rigorous" approach. However, if the product solids content was higher (i.e., water content lower) than that predicted by the theoretical flash, the yield calculated by the flash method was greater than

that calculated by the other procedures. This would typically occur for runs in which the pressure within the reactor was not maintained at a level above the equilibrium vapour pressure of water at the reaction temperature. Therefore, the flash calculation would not apply in these circumstances because more water evaporated from the product than was predicted by theory.

The other scenario took place when the product dry solids were lower (i.e., more water) than was predicted by the flash calculation. In this case, the yield determined by the flash method was lower than that calculated by the other procedures. Such a situation typically occurred when the reaction conditions were harsh, and volatiles which were not detected as product solid were produced in significant amounts. Hence, the measured volume of water in the product (from oven-dry solids), was falsely high. Thus, the yield calculated by the "rigorous" method above was also high. Under such conditions, perhaps more value should be placed in the yield calculated using flash factors.

iv) Examples

The magnitude of the differences between the three calculation methods described above may be shown by examining some examples from our experimental runs, as outlined in the following table.

Experimental Run	Description	Glucose/Initial Cellulose Yields (%)		
		Original (i)	Rigorous (ii)	Flash (iii)
Z	no degrad; flash>theory	50.1	50.0	55.0
2V	no degrad; flash=theory	45.0	44.8	44.3
2A	degrad; flash<theory	59.7	55.1	53.5
3D	degrad; flash<theory	24.3	20.5	19.1

There is virtually no difference between yield calculations (i) and (ii) when very small quantities of sugar degradation products are detected (e.g., runs Z and 2V). However, in runs in which the reaction conditions were quite harsh and significant levels

of sugar degradation products were detected, the rigorous yield (ii) is noticeably lower than that calculated by the original method (i) (e.g., runs 2A and 3D).

In run 2V the measured flash was very similar to the theoretical flash and as a result yield (iii) was almost identical to those calculated by the other methods. When the measured flash was greater than that predicted by theory (e.g., run Z), yield (ii) was less than that calculated using the theoretical flash factor (yield (iii)). Conversely, when the measured flash factor was less than that predicted by theory, as in runs 2A and 3D, the rigorous yield was greater than the flash yield.

APPENDIX B

HYDROLYSIS EXPERIMENTAL DATA

B.1 Log Sheet of Plug Flow Hydrolysis Runs

Appendix B.1

Table B.1

Log Sheet of Plug Flow Hydrolysis Runs

Run	Description	Reaction T (C)	Res. Time (min)	Acid/Wood (w/w)	%HCl in Sol'n	Glu/Cell Yield (%) (corrected)	% Glu/Cell (using flash to calc H20)	FEED D.S. (%)	pH feed	REACTION CONDITIONS Acid Rate (mL/min)	Rxn. Zone(ft)	PRODUCT D.S. (%)	pH (meas'd)	Meas. Flow (lb/min)	Corr. Flow (kg/min)	Theor Flash Factor(%)	Hydrol. GLU concn. (g/L) (HPLC)	Cell Conv. to HMF (%)	Cell Conv. to LEV & FOR (%)	EC50 (% glu)
SW - H	1st acid inj; high t,mod. T,low acid	221	2.3	0.011	0.20	30.9	31.4	13.5	2.1	24	120	17.4	1.42	13.5	7.7	23.40	32.0	0.00	0.00	>10
SW - I	high t, low T, low acid	215	2.2	0.012	0.20	29.2	32.6	12.7	2.1	25	120	17.5	1.30	14.3	8.0	22.20	30.5			>8
SW - J	high t,high T,low A double run with I	226	2.3	0.010	0.16	34.5	37.3	12.7	2.1	18	120	17.4	1.35	13.5	7.8	24.00	35.7			>8
SW - K	water backup from HAGI dilute feed, T	220	2.8	-0.02	0.20	34.8	55.4	6.9	2.3	25	120	13.5	1.28	10.9	6.3	23.10	26.7			8
	change as run progres	210	2.3	-0.02	0.17	14.5	23.8	6.9	2.3	25	120	11.0	1.20	13.5	7.6	21.20	11.2			
SW - L	water backup again higher acid	218	2.6	0.025	0.24	43.1	50.6	8.8	2.35	35	120	13.0	1.00	12.0	6.9	22.50	31.5			>8
SW - M	Control Run; no acid injection	220	2.7	0.001	0.03	13.7	16.8	21.5	2.2	0	120	30.6	2.35	11.8	6.5	23.20	30.0	0.00	0.00	>8

APPENDIX B.1 (cont'd)

Run	Description	Reaction T (C)	Res. Time (min)	Acid/Wood (v/v)	%HCl in Sol'n	Glu/Cell Yield (%) (corrected)	% Glu/Cell (using flash to calc H20)	FEED D.S. (%)	pH feed	REACTION CONDITIONS Acid Rate (mL/min)	Rxn. Zone(ft)	PRODUCT D.S. (%)	pH (meas'd)	Meas. Flow (lb/min)	Corr. Flow (kg/min)	Theor Flash Factor(%)	Hydrol. GLU concn. (g/L) (HPLC)	Cell Conv. to HMF (%)	Cell Conv. to LEV & FOR (%)	EC50 (% glu)
SW - N	high t, mod. T, low A 2xA @ 1/2 conc	219	2.5	0.011	0.29	50.9	54.0	21.5	2.2	80	120	27.6	1.16	12.8	7.1	23.00	96.0	2.95	2.15	7
SW - O	high t, low T, low A	215	2.6	0.010	0.28	46.5	48.1	21.5	2.2	75	120	27.0	1.14	12.5	6.9	22.20	84.6	1.70	1.07	>8
SW - R	repeat of SW-P	216	2.2	0.027	0.72	51.6	51.1	21.1	2.15	250	120	25.0	0.72	15.0	8.3	22.40	88.0	5.35	8.60	2
SW - S	low t, low T, low A first run w 1 coil	207	0.9	0.016	0.28	20.4	27.2	15.2	2.3	77	40	23.3	1.10	11.5	6.3	20.60	30.7			
SW - T	low t, low T, high A	207	1.0	0.050	0.88	36.4	38.4	15.2	2.3	250	40	19.5	0.53	11.2	6.2	20.60	43.3			6
SW - U	MODERATE RUN 2 coils, mod T, mod A	217	1.9	0.026	0.60	50.2	54.2	18.8	2.25	164	80	24.0	0.66	11.4	6.3	22.60	81.0	6.05	8.05	4
SW - V	MODERATE RUN 2 coils, mod T, mod A	220	2.2	0.028	0.64	49.7	50.4	18.8	2.25	150	80	21.9	0.65	9.7	5.4	23.20	75.9	7.24	19.67	4
SW - W	MODERATE RUN 2 coils, mod T, mod A	213-216	1.6	0.020	0.49	46.3	46.0	19.8	2.15	166	80	24.1	0.78	15.3	8.4	22.00	72.8	1.63	2.49	
SW - X	MODERATE RUN 2 coils, mod T, mod A	220	1.5	0.021	0.51	50.5	47.7	19.8	2.15	164	80	23.2	0.73	14.3	8.0	23.20	76.7	4.41	5.06	
SW - Z	1 coil, high T, low A	226	0.8	0.011	0.27	50.0	55.0	20.1	2.25	77	40	27.3	1.10	13.1	7.4	24.50	91.7	1.48	0.00	
SW - ZA	1 coil, high T,high A	227	0.8	0.032	0.81	55.1	52.1	20.1	2.25	250	40	23.1	0.58	13.1	7.4	24.70	87.1	12.61	12.64	2
SW - ZB	1 coil, low T, low A	216	0.7	0.009	0.22	27.6	31.2	19.8	2.30	67	40	26.7	1.30	14.4	8.0	22.40	49.6			12

APPENDIX B.1 (cont'd)

Run	Description	Reaction T (C)	Res. Time (min)	Acid/Wood (w/w)	%HCl in Sol'n	Glu/Cell Yield (%) (corrected)	% Glu/Cell (using flash to calc H2O)	FEED D.S. (%)	pH feed	REACTION CONDITIONS Acid Rate (mL/min)	Rxn. Zone(ft)	PRODUCT D.S. (%)	pH (meas'd)	Meas. Flow (lb/min)	Corr. Flow (kg/min)	Theor Flash Factor(%)	Hydrol. GLU concn. (g/L) (HPLC)	Cell Conv. to HMF (%)	Cell Conv. to LEV & FOR (%)	EC50 (% glu)	
SW - 2C3	3 coils, high T,low A	225	5.8	0.026	0.58	36.1	40.7	19.7	2.27	75	120	24.8	0.95	5.5	3.1	24.30	65.9	12.97	19.98	2	
SW - 2C4		225	5.0	0.021	0.50	39.4	50.0	19.7	2.27	75	120	27.3	0.85	6.4	3.6	24.30	81.0	8.31	19.56		
SW - 2C5		224	4.2	0.018	0.43	47.0	57.9	19.7	2.27	75	120	27.3	0.90	7.5	4.2	24.10	93.5	7.30	14.39		
SW - 2C7		223	3.5	0.015	0.37	52.1	56.1	19.7	2.27	75	120	24.5	1.05	9.0	5.1	23.90	90.4	6.99	16.59		
SW - 2C8		223	3.5	0.015	0.36	53.3	55.2	19.7	2.27	75	120	24.3	0.95	9.1	5.1	23.90	88.9	7.25	11.23		
SW - 2C9		223	3.5	0.015	0.36	51.9	53.0	19.7	2.27	75	120	24.1	0.95	9.1	5.1	23.90	85.4	6.95	10.86		
SW - 2D	3 coils, high T,high A	Temperature fell off drastically - boiler trouble																			
SW - 2D4	3 COIL, LO T, HI A	215	2.6	0.028	0.77	44.3	47.7	21.4	2.20	216	120	26.7		12.5	6.9	22.20	83.4	4.44	9.87		
SW - 2E	3 coils, high T,high A	Temperature fell off drastically - boiler trouble																			
SW - 2E4	3 COIL, MOD T, HI A	219	3.4	0.040	0.98	37.4	49.0	19.8	2.20	218	120	28.0		9.5	5.3	23.00	78.6	2.51	18.09		
SW - 2K	1 coil, low T, high A																				
SW - 2K3	mod-high T	222	1.1	0.033	0.78	21.3	19.7	19.1	2.20	175.0	40	20.0		9.5	5.3	23.60	30.4	3.15	26.58		
SW - 2K4	low T	216-204	0.9	0.026	0.61	33.7	31.5	19.1	2.20	175.0	40	21.4		12.5	6.8	21.00	47.0	0.00	8.40		
SW - 2K7	high T	230	1.2	0.035	0.82	5.6	5.2	19.1	2.20	175.0	40	18.7		8.9	5.1	25.30	8.2	0.00	42.52		
SW - 2L	MODERATE RUN																				
SW - 2L4	2 coil,mod T,mod A	220	1.3	0.012	0.30	46.9	49.8	20.0	2.20	113.0	80	25.0		17.0	9.5	23.20	81.0	7.22	10.11		
SW - 2M	MODERATE RUN																				
SW - 2M3	2 coil,mod T,mod A	221	1.4	0.017	0.44	42.8	41.9	20.2	2.20	155.0	80	23.4		15.6	8.7	23.40	69.3	5.32	14.57	6	
SW - 2N	MODERATE RUN																				
SW - 2N3	2 coil,mod T,mod A	218	1.3	0.017	0.43	41.2	41.2	20.6	2.20	155.0	80	24.5		16.3	9.0	22.80	69.2	3.60	10.07		
SW - 2O	1 coil,lo T,hi A																			6	
SW - 202	lo T	215	0.7	0.027	0.62	48.6	47.6	18.4	2.20	230.0	40	21.7		16.0	8.9	22.20	69.0	2.62	9.24		
SW - 203	lo-mod T	217	0.9	0.034	0.78	37.7	36.2	18.4	2.20	230.0	40	20.3		12.5	7.0	22.60	52.7	7.73	19.70		

APPENDIX B.1 (cont'd)

Run	Description	Reaction T (C)	Res. Time (min)	Acid/Wood (w/w)	%HCl in Sol'n	Glu/Cell Yield (%) (corrected)	% Glu/Cell (using flash to calc H20)	FEED D.S. (%)	pH feed	REACTION CONDITIONS Acid Rate (mL/min)	Rxn. Zone(ft)	PRODUCT D.S. (%)	pH (meas'd)	Meas. Flow (lb/min)	Corr. Flow (kg/min)	Theor Flash Factor(%)	Hydrol. GLU concn. (g/L) (HPLC)	Cell Conv. to HMF (%)	Cell Conv. to LEV & FOR (%)	EC50 (% glu)
SW - 2P	FUEL CHIPS																			
SW - 2P4	1 coil,lo T,lo A	193	0.6	0.006	0.11	0.5	0.6	16.4	3.90	52.0	40	21.2	2.00	19.6	10.4	17.50	0.7 (YSI)			
SW - 2Q	FUEL CHIPS																			
SW - 2Q4	3 COIL,mod T,lo A	213-205	2.1	0.009	0.20	2.9	3.7	19.2	3.55	75.0	120	27.7	2.30	15.6	8.5	21.00	5.5 (YSI)			
SW - 2R	FUEL CHIPS																			
	3 COIL,mod T,lo A	215-211	2.3	0.020	0.45	8.9	11.2	18.3	3.7	158.0	120	26.7	1.40	14.3	7.9	22.00	16.1			
SW - 2S	Upgraded Boiler																			
SW - 2S4	3 coil,mod-hi T,lo A	220-224	2.6	0.011	0.26	34.9	33.8	18.6	2.8	76.0	120	21.0	1.25	12.4	6.9	23.40	50.4	8.54	17.77	
SW - 2S5	NO ACID IN FEED TK	217-222	2.1	0.009	0.21	46.3	46.2	18.6	2.8	76.0	120	22.1	1.25	14.9	8.3	23.00	68.5	11.92	10.11	
SW - 2S6	(pine)	217-227	2.0	0.009	0.20	45.1	44.1	18.6	2.8	76.0	120	22.0	1.25	16.0	9.0	23.60	66.0	6.68	10.22	
SW - 2T																				
SW - 2T4	3 coil,mod-hi T,lo A	217-224	2.7	0.009	0.21	40.8	39.0	18.6	2.35	56.0	120	20.7	1.25	12.0	6.7	23.20	58.0	8.51	18.48	
SW - 2T5	ACID IN FEED TK	214-225	2.5	0.009	0.20	49.2	45.2	18.6	2.35	56.0	120	21.9	1.25	12.5	7.0	23.20	67.3			
SW - 2T6		214-225	1.7	0.006	0.14	47.9	45.4	18.6	2.35	56.0	120	22.4	1.30	18.3	10.2	23.20	67.5			
SW - 2U	1 coil,hi T, lo A																			12
SW - 2U4	No Acid in Feed	229	0.6	0.008	0.17	56.8	56.6	18.4	2.9	73.5	40	23.0	1.35	17.8	10.1	25.10	85.2	9.26	4.38	
SW - 2U5		228	0.6	0.008	0.18	54.7	52.0	18.4	2.9	73.5	40	22.3	1.30	17.1	9.8	24.90	78.0	6.13	2.84	
SW - 2V	1 coil,hi T, lo A																			
SW -2V3	higher pump speed	229	0.5	0.008	0.17	44.8	44.3	18.6	2.85	95.2	40	23.5	1.32	22.8	13.0	25.10	67.6	1.96	0.56	
SW - 2V	1 coil,hi T, lo A																			
SW - 2V4	0.10" ORIFICE	228	0.6	0.010	0.21	58.4	53.5	17.0	2.9	88.5	40	20.2	1.25	17.3	9.9	24.90	73.0	8.33	1.56	
SW - 2X	1 coil,hi T, lo A																			
SW - 2X3	NEW 0.15" orif	230	0.6	0.012	0.24	48.5	50.9	16.9	2.9	109.0	40	22.2	1.20	18.3	10.5	25.30	69.3	5.49	4.01	

APPENDIX B.1 (cont'd)

Run	Description	Reaction T (C)	Res. Time (min)	Acid/Wood (w/w)	%HCl in Sol'n	Glu/Cell Yield (%) (corrected)	% Glu/Cell (using flash to calc H2O)	FEED D.S. (%)	REACTION CONDITIONS pH feed	Acid Rate (mL/min)	Rxn. Zone(ft)	PRODUCT D.S. (%)	pH (meas'd)	Meas. Flow (lb/min)	Corr. Flow (kg/min)	Theor Flash Factor(%)	Hydrol. GLU concn. (g/L) (HPLC)	Cell Conv. to HMF (%)	Cell Conv. to LEV & FOR (%)	ECSO (% glu)
SW - 2Y	1 coil,hi T, lo A NEW 0.15" orif & stator	230	0.7	0.007	0.20	48.5	53.6	21.1	3.1	68.0	40	28.8	1.22	14.5	8.2	25.30	96.0	2.08	0.00	8
SW - 2Z	1 coil,hi T, lo A	233	0.7	0.012	0.29	55.9	59.0	19.7	3.15	104.0	40	26.0	1.15	14.8	8.5	26.00	97.8	6.91	3.27	6
SW - 3A	1 coil,hi T, lo A																			
SW-3A-3	-- low flow	230	0.8	0.014	0.30	50.5	46.4	17.6	2.85	103.0	40	28.2	1.10	13.8	7.9	25.30	66.3	15.00	9.37	
SW - 3B	1 coil,hi T, lo A																			
SW-3B-3	new stator, good flow but pump failed	225-230	0.6	0.006	0.15	39.9	42.9	21.3	3.00	61.0	40	28.0	1.15	17.0	9.6	24.70	77.1	1.73	2.39	6
SW - 3C	3 coil, hi T, hi A																			
SW-3C-4		230	3.6	0.039	1.03	0.7	0.7	21.0	2.80	217.0	120	20.7	0.50	8.8	5.0	25.30	1.2	0.00	43.95	
SW-3C-5		230	3.4	0.038	0.80	1.1	1.0	21.0	2.80	217.0	120	20.5	0.50	8.9	5.0	25.30	1.9	0.00	48.09	
SW - 3D	3 coil, hi T, hi A new stator, plated rotor	228	1.9	0.020	0.54	20.5	19.1	21.5	3.15	211.0	120	22.5	1.05	16.5	9.3	24.90	34.8	4.54	30.24	2
SW - 3E	3 coil, mod T, lo A	217-220	1.8	0.010	0.25	51.7	50.9	20.0	2.85	104	120	24.2	1.40	18.0	10.0	22.90	82.5	0.00	5.69	6

APPENDIX B.1 (cont'd)

Run	Description	Reaction T (C)	Res. Time (min)	Acid/Wood (w/w)	%HCl in Sol'n	Glu/Cell Yield (%) (corrected)	% Glu/Cell (using flash to calc H2O)	FEED D.S. (%)	pH feed	REACTION CONDITIONS Acid Rate (mL/min)	Rxn. Zone(ft)	PRODUCT D.S. (%)	pH (meas'd)	Meas. Flow (lb/min)	Corr. Flow (kg/min)	Theor Flash Factor(%)	Hydrol. GLU concn. (g/L) (HPLC)	Cell Conv. to HMF (%)	Cell Conv. to LEV & FOR (%)	ECSO (% glu)
SW - 3F	1 coil,hi T, lo A																			
SW-3F-2		228	0.5	0.006	0.15	47.5	55.2	20.1	2.80	75	40	28.1	1.40	21.4	12.1	24.90	92.2	2.59	2.62	
SW-3F-3		228	0.5	0.007	0.17	49.2	57.9	20.1	2.80	84	40	28.3	1.35	21.0	11.9	24.90	96.6	4.53	2.80	
SW - 3G	1 coil,hi T, lo A																			
SW-3G-4	LONG RUN	232	0.5	0.007	0.19	45.3	45.3	20.6	2.90	92	40	26.3	1.40	20.0	11.4	25.7	79.1	0.00	0.00	
SW-3G-5		232	0.5	0.007	0.18	47.9	46.6	20.6	2.90	92	40	25.8	1.30	22.0	12.5	25.7	81.3	0.00	0.00	
SW-3G-6		220	0.5	0.006	0.18	41.9	41.0	22.1	2.90	95	40	27.0	1.25	23.0	12.7	23.2	75.8	0.00	0.00	6
SW-3G-7		218	0.5	0.007	0.19	43.6	40.9	22.1	2.90	97	40	26.0	1.25	23.0	12.7	22.6	74.9	0.00	0.00	
SW - 3H	1 coil,hi T, lo A																			
SW-3H-3	LONG RUN	229	0.6	0.008	0.21	53.9	51.2	20.2	2.90	94.2	40	24.8	1.30	18.8	10.6	25.1	86.5	0.00	0.00	
SW-3H-4		221	0.5	0.008	0.20	44.2	46.4	20.2	2.90	94.2	40	26.2	1.25	20.3	11.3	23.4	76.7	0.00	0.00	
SW-3H-5		217	0.5	0.007	0.19	44.1	44.5	20.9	2.90	94.2	40	26.1	1.23	21.5	11.9	22.8	76.2	0.00	0.00	8

B.2 Statistical Analysis of Hydrolysis Experiments

Appendix B.2

Table B.2
Statistical Analysis of Hydrolysis Experiments

Contrast Matrix for 2^3 Factorial Experiment

PINE CELLULOSE HYDROLYSIS EXPTS. FOR SEDF
A-TEMPERATURE, B-TIME, C-% HCl IN SOLN.
Uses replicate runs to contribute to SSE

No. of Replications= 1

Experiment	Treatment Combination	Treatment Total	(1)	(2)	(3)	Sum of Squares
2B	(1)	24.8	69.8	158.4	316.6	
Z	a	45.0	88.6	158.2	3.0	1.13
O	b	41.9	93.3	25.0	-9.6	11.52
2C	ab	46.7	64.9	-22.0	-49.2	302.58
2O	c	43.7	20.2	18.8	-0.2	0.00
2A	ac	49.6	4.8	-28.4	-47.0	276.13
R	bc	46.4	5.9	-15.4	-47.2	278.48
3D	abc	18.5	-27.9	-33.8	-18.4	42.32

Analysis of Variance Table

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Theoretical f
Main Effect					
A	1.13	1	1.13	0.08	7.71 (5% level)
B	11.52	1	11.52	0.77	21.20 (1% level)
C	0.00	1	0.00	0.00	
2-Factor					
AB	302.58	1	302.58	20.33	
AC	276.13	1	276.13	18.55	
BC	278.48	1	278.48	18.71	
3-Factor					
ABC	42.32	1	42.32	2.84	
Error	59.55	4	14.89		
Total	971.70	11			

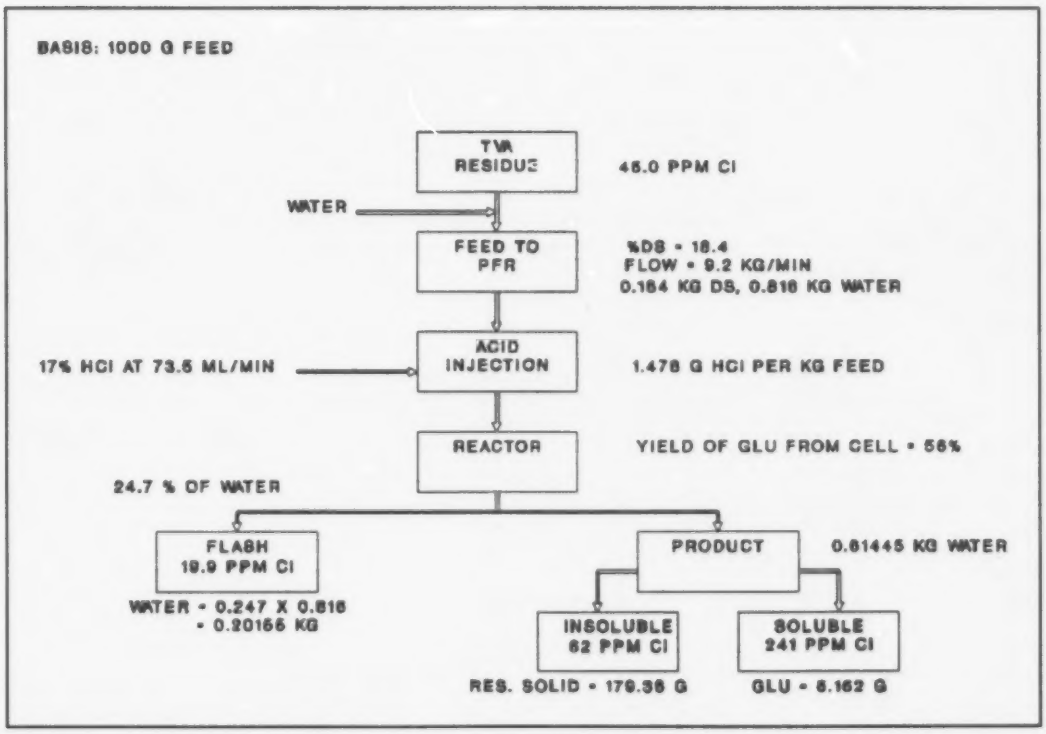
Appendix B.3

Chloride Balance for Run 2U

Chloride Analysis Results:

TVA Prehydrolysed Pine Residue: 45.0 ppm Cl^-
Insoluble Residue from Product Washing : 62 ppm Cl^- *
Soluble Stream from Product Washing: 266 ppm Cl^- **

* Product (22.3% dry solids) weighing 98.93 g was washed to produce a soluble fraction with a volume of 740 mL.
** A background Cl^- of 25 ppm was used in the calculation (therefore 241 ppm Cl^- from product itself); this figure comes from the Ministry of Environment survey of Toronto drinking water.



HCl BALANCE Basis: feed = 1000 g

1. TVA Pine Residue

45.0 ppm Cl^- (46.3 ppm HCl) in dry material =

$$46.3 \frac{\text{mg HCl}}{\text{kg DS}} \times 0.184 \text{ kg DS} = 8.513 \text{ mg} = 0.0085 \text{ g HCl}$$

2. HCl Injection

$$1.478 \frac{\text{g HCl}}{\text{kg feed}} = 1.478 \text{ g HCl}$$

3. Flash Steam

19.85 ppm Cl^- (20.4 ppm HCl) =

$$20.4 \frac{\text{mg HCl}}{\text{kg } H_2O} \times 0.2015 \text{ kg } H_2O = 4.113 \text{ mg} = 0.0041 \text{ g HCl}$$

4. Product (%DS = 22.3)

98.93 g product washed = 22.06 g DS + 76.87 g H_2O

a)Soluble Stream

241 ppm Cl^- = 247.8 ppm HCl
Volume = 740 mL
weight of HCl in sample

$$= 247.8 \frac{\text{mg HCl}}{\text{L}} \times 0.740 \text{ L}$$

$$= 183.36 \text{ mg HCl}$$

$$\frac{0.18336 \text{ g HCl}}{0.07687 \text{ L } H_2O} = 2.385 \frac{\text{g HCL}}{\text{L}}$$

$$= 2.385 \frac{\text{g HCl}}{\text{L}} \times 0.61445 \text{ L}$$

$$= 1.465 \text{ g HCl}$$

b)Insoluble Stream

$$62 \text{ ppm } Cl^- = 63.7 \text{ ppm HCl} = 63.7 \frac{\text{mg HCL}}{\text{kg DS}} \times 0.17936 \text{ kg DS}$$

$$= 11.425 \text{ mg HCl}$$

$$= 0.0114 \text{ g HCl}$$

Balancing these numbers:

Feed	+ Injected	= Sol. Product	+ Insol. Product	+ Flash
0.0085 g	+ 1.478 g	= 1.465 g	+ 0.0114 g	+ 0.0041 g
	1.4865 g HCl	= 1.4805 g HCl		

Therefore it appears that 99.1% of the injected HCl ends up in the soluble product stream, making HCl recovery through the flash steam impossible.

Appendix B.4

Swedish Pilot-Scale Dryer Tests

Procedural Details:

-For each batch, approximately 26 kg (50/50 mixture of wet and recycled product) was fed to the dryer.
-The residence time for each run was about 15 minutes.
-The feed rate was thus approximately 100 kg/hour.
-Some of the product from each pass was bled off.
-The system pressure in the dryer was 0.25-0.30 bar (gauge).
-The tube side of the heat exchangers was supplied with 8 bar (gauge) steam, T=175 °C.
-The velocity inside the heat exchanger tubes was 25 m/sec.
-The configuration of the dryer was the shortest possible resulting in a solids residence below 10 seconds.
-The product seemed to be somewhat overdried, more than 95% DS.
-The DS content of wet second stage sludge was once determined to be 24-25%.
-Condensate sample from evaporated steam was collected during pass 2 batch 4.
-All dried product was sent to the SEDF in Örnsköldsvik, Sweden.

Table B.3. Structure of the pilot scale dryer experiments

Log time (min)	Batch No.	M_{rec} (kg)	M_{moist} (kg)	M_{mix} (kg)	M_{prod} (kg)	DS_{mix} (%)	DS_{prod} (%)
Stage 1:							
35	-	- +	60	-	28	48.7	-
Stage 2:							
84	1	14.2 +	14	28	-	57.7	-
110	2	13.2 +	13.2	24.3	13.8	61.5	-
138	3	12.5 +	14	26.2	15.5	59.1	-
172	4	12.5 +	14	26	15.5	59.1	-
201	5	12.5 +	14	25.5	14.5	-	97.1
228	6	12.5 +	13.8	26	14.5	-	-
257	7	12.5 +	14.4	27.2	16	58.4	-

		Sum =	97.4 kg	fresh sludge from stage 2			

M_{rec} weight of dried, recycled material included in the feed
M_{moist} weight of fresh (wet) hydrolysis residue included in the feed
M_{mix} total weight of the feed mixture
M_{prod} total weight of dried product for the specified batch
DS_{mix} dry solids content of the feed mixture
DS_{prod} dry solids content of the product

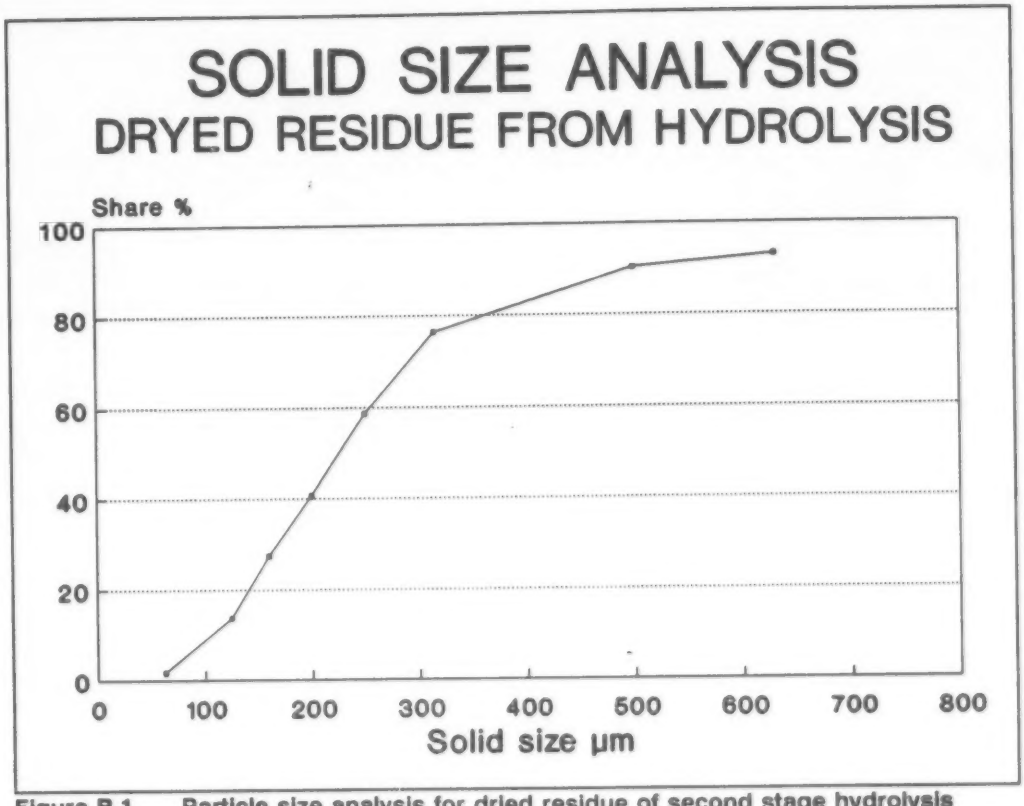


Figure B.1. Particle size analysis for dried residue of second stage hydrolysis

APPENDIX C

LAB- AND PILOT-SCALE FERMENTATION DATA

Appendix C

Lab- and Pilot-scale Fermentation Data

Table C.1

MULTIGEN FERMENTATION -- ~5% Synthetic Control (with condenser)

Time (hr)	OD (620 nm)	Log OD	Glu-ox. Glucose (g/L)	Ethanol (g/L)	GC Sugar Profile Arabinose (g/L)	Xylose (g/L)	Mannose (g/L)	Glucose (g/L)	Galactose (g/L)	Ferment'l Sugars (g/L)	Sugar Used (g/L)	Yield (EtOH/ Sugar) (g/g)	Rate of Sugar Use (g/L/hr)	Rate of Alcohol Prod'n (g/L/hr)	Yp/s
0	0.89	-0.05		0.03	1.69	4.75	9.29	30.06	2.86	39.35					
4	1.11	0.05		0.15	1.56	4.38	9.53	29.25	2.84	38.78	0.57	0.26			
7	1.98	0.30		0.54	1.67	4.87	9.17	29.09	3.13	38.26	1.09	0.50			
9.75	3.94	0.60		1.77	1.71	4.85	9.63	27.87	2.66	37.50	1.85	0.96			
21	18.60	1.27		15.06	1.57	4.40	0.83	0.06	1.29	0.89	38.46	0.39	3.25	1.18	0.36
23	18.60	1.27		19.29	1.54	4.37	0.29	0.00	0.00	0.29	39.06	0.49			
26	19.30	1.29		19.18	1.68	4.55	0.06	0.03	0.00	0.09	39.26	0.49			
31.2	20.80	1.32		18.72	1.52	4.15	0.06	0.03	0.00	0.09	39.26	0.48			
53.5	19.30	1.29		15.43	1.16	2.89	0.04	0.00	0.00	0.04	39.31	0.39			
77.5	20.20	1.31		16.90	1.09	2.79	0.03	0.00	0.00	0.03	39.32	0.43			

** Condenser and stirrer off by 53.5 hr, not sure when it failed.

Table C.2

MULTIGEN FERMENTATION -- ~8% Synthetic Control (with condenser)

Time (hr)	OD (620 nm)	Log OD	Glu-ox. Glucose (g/L)	Ethanol (g/L)	GC Sugar Profile Arabinose (g/L)	Xylose (g/L)	Mannose (g/L)	Glucose (g/L)	Galactose (g/L)	Ferment'l Sugars (g/L)	Sugar Used (g/L)	Yield (EtOH/ Sugar) (g/g)	Rate of Sugar Use (g/L/hr)	Rate of Alcohol Prod'n (g/L/hr)	Yp/s
0	1.1	0.02	52.70	0.06	2.88	8.34	22.70	49.35	4.69	72.05					
6.5	2.42	0.38	49.59	1.14	2.98	7.00	22.45	45.67	4.88	68.12	3.93	0.29			
12.5	9.49	0.98	40.40	6.68	2.89	8.23	20.13	37.12	5.15	57.25	14.80	0.45			
22	15.54	1.19	14.00	18.77	2.63	7.62	14.43	12.32	3.82	26.75	45.30	0.41			
24.5	14.34	1.16	9.47	21.14	2.61	7.12	12.50	7.78	3.74	20.28	51.77	0.41	3.12	1.22	0.39
27	14.94	1.17		21.88	3.27	8.33	12.51	6.95	5.10	19.46	52.59	0.42			
31	18.94	1.28		23.78	3.19	8.26	10.16	2.94	5.24	13.10	58.95	0.40			
47	18.54	1.27		29.08	2.76	7.32	0.29	0.04	1.57	0.33	71.72	0.41			
50	19.34	1.29		31.39	2.51	6.55	0.12	0.00	0.31	0.12	71.93	0.44			
54				30.18	2.44	6.53	0.08	0.00	0.00	0.08	71.97	0.42			

Based on linear regression, 12.5-->24.5 hr

Table C.3

MULTIGEN FERMENTATION -- -5% 3G/TVA MIX (with condenser)

Time (hr)	OD (620 nm)	Log OD	Glu-ox. Glucose (g/L)	Ethanol (g/L)
0	1.5	0.18	31.21	0.15
4.5	2.6	0.41	29.70	1.03
19	14.2	1.15	3.74	14.49
23.5	18.6	1.27	0.20	17.07
28.5	23.0	1.36	0.00	19.23
50.5	22.4	1.35	0.00	22.00

GC Sugar Profile				
Arabinose (g/L)	Xylose (g/L)	Mannose (g/L)	Glucose (g/L)	Galactose (g/L)
1.96	5.49	15.18	31.85	3.16
1.79	5.23	14.13	28.56	3.02
1.41	4.13	7.38	4.86	1.64
1.93	5.40	6.03	1.66	2.76
1.76	4.97	3.24	0.09	2.17
1.67	4.52	0.44	0.05	0.14

Ferment'l Sugars (g/L)	Sugar Used (g/L)	Yield (EtOH/ Sugar) (g/g)
47.03		
42.69	4.34	0.24
12.24	34.79	0.42
7.69	39.34	0.43
3.33	43.70	0.44
0.49	46.54	0.47

Based on two points 4.5 and 19 hr

Rate of Sugar Use (g/L/hr)	Rate of Alcohol Prod'n (g/L/hr)	Yp/s
2.10	0.93	0.44

Table C.4

MULTIGEN FERMENTATION -- -8% 3G/TVA MIX (with condenser)

Time (hr)	OD (620 nm)	Log OD	Glu-ox. Glucose (g/L)	Ethanol (g/L)
0	2.3	0.36	50.30	0.17
5.5	3.3	0.52	47.65	0.99
17	8.5	0.93	31.33	6.73
21	7.6	0.88	28.63	9.559
24.5	9.1	0.96	20.45	13.80
29.5	12.0	1.08	5.93	22.23
40.5	19.7	1.29	0.10	30.12
43	18.6	1.27	0.08	27.82
47	17.8	1.25		29.66
50.5	18.5	1.27		27.93
69.75	19.4	1.29		31.90
115	20.6	1.31		27.76

GC Sugar Profile				
Arabinose (g/L)	Xylose (g/L)	Mannose (g/L)	Glucose (g/L)	Galactose (g/L)
3.23	9.41	19.55	49.83	4.19
2.90	9.18	19.44	46.30	4.70
3.10	8.53	19.26	35.10	3.68
2.92	8.71	16.82	28.75	3.61
2.85	8.26	15.82	22.48	4.58
2.58	8.36	14.41	9.15	3.62
2.69	8.20	7.97	1.00	3.99
2.36	7.45	4.39	0.18	3.48
2.06	6.32	1.00	0.10	2.99
2.11	6.10	0.13	0.07	1.63

Ferment'l Sugars (g/L)	Sugar Used (g/L)	Yield (EtOH/ Sugar) (g/g)
69.38		
65.74	3.64	0.27
54.36	15.02	0.45
45.57	23.81	0.40
38.30	31.08	0.44
23.56	45.82	0.49
8.97	60.41	0.50
4.57	64.81	0.43
1.10	68.28	0.47
0.20	69.18	0.40

Based on linear regression, 17-->29.5 hr

Rate of Sugar Use (g/L/hr)	Rate of Alcohol Prod'n (g/L/hr)	Yp/s
2.62	1.25	0.48

Table C.5

MULTIGEN FERMENTATION -- ~8% 3H/TVA MIX (with condenser)

Time (hr)	OD (620 nm)	Log OD	Glu-ox. Glucose (g/L)	Ethanol (g/L)	GC Sugar Profile Arabinose (g/L)	Xylose (g/L)	Mannose (g/L)	Glucose (g/L)	Galactose (g/L)	Ferment'l Sugars (g/L)	Sugar Used (g/L)	Yield (EtOH/ Sugar) (g/g)
0	1.6	0.20	51.13	0.17	2.65	8.37	23.08	50.49	5.22	73.57		
10.5	6.45	0.81	44.25	3.25	3.00	8.96	22.19	49.86	5.74	72.05	1.52	2.14
14.5	6.45	0.81	36.60	5.54	3.00	7.97	20.50	40.41	4.12	60.91	12.66	0.44
18.5	8.85	0.95	30.80	9.36	2.70	8.20	18.88	30.20	5.42	49.08	24.49	0.38
20	14.15	1.15	25.92	11.44	2.36	7.31	16.73	24.81	4.45	41.54	32.03	0.36
34.25	21.75	1.34	1.53	26.09	2.78	12.21	11.09	3.99	4.98	15.08	58.49	0.45
38	20.25	1.31	1.16	28.10	2.67	11.73	9.52	1.97	4.27	11.49	62.08	0.45
41	21.05	1.32		28.22	2.54	10.29	8.84	1.07	4.24	9.91	63.66	0.44
44	21.65	1.34		30.41	2.70	11.49	7.59	0.58	4.03	8.17	65.40	0.46
58.5	22.95	1.36		31.96	2.15	9.62	3.31	0.04	3.74	3.35	70.22	0.46
61.5	22.35	1.35		32.02	2.20	9.69	3.16	0.04	4.12	3.20	70.37	0.46
65.5				29.94	2.32	9.50	2.27	0.00	3.62	2.27	71.30	0.42

Based on linear regression, 14.5-->34.25 hr

Rate of Sugar Use (g/L/hr)	Rate of Alcohol Prod'n (g/L/hr)	Yp/s
2.37	1.04	0.44

Table C.6

PILOT PLANT RUN #1 -- ~6% 3G/TVA MIX (no condenser, temp ~26-28 deg.)

Time (hr)	OD * (620 nm)	Log OD	Glu-ox. Glucose (g/L)	Ethanol (g/L)	GC Sugar Profile Arabinose (g/L)	Xylose (g/L)	Mannose (g/L)	Glucose (g/L)	Galactose (g/L)	Ferment'l Sugars (g/L)	Sugar Used (g/L)	Yield (EtOH/ Sugar) (g/g)
0	1.13	0.05		0.39	1.94	6.46	15.04	38.36	4.04	53.40		
6.8	1.45	0.16		0.80	1.99	6.30	14.17	37.19	3.92	51.36	2.04	0.39
16.75	3.33	0.52		4.34	2.51	8.00	15.40	33.46	3.50	48.86	4.54	0.96
21	5.93	0.77		8.13	2.47	7.52	13.83	23.26	3.16	37.09	16.31	0.50
25				10.80	2.46	7.02	12.88	14.06	3.96	26.94	26.46	0.41
33	6.78	0.83		14.63	2.03	6.46	8.36	3.06	3.35	11.42	41.98	0.35
41.3	10.08	1.00		14.05	2.05	6.37	4.08	0.24	3.49	4.32	49.08	0.29
45.8	8.58	0.93		14.74	1.85	5.82	1.50	0.16	2.76	1.66	51.74	0.28
48	7.58	0.88		13.65	1.61	5.33	0.87	0.13	2.75	1.00	52.40	0.26
67	17.08	1.23		7.14	1.49	4.17	0.05	0.08	0.30	0.13	53.27	0.13
114	21.08	1.32										

Based on linear regression, 16.75-->33 hr

Rate of Sugar Use (g/L/hr)	Rate of Alcohol Prod'n (g/L/hr)	Yp/s
2.285	0.62	0.27

* Note: ODs were measured on samples that had been frozen, and then thawed.

Table C.7

PILOT PLANT RUN #2 -- ~6% 3G/TVA (with condenser, although not completely effective)

Time (hr)	OD* (620 nm)	Log OD	Glu-ox. Glucose (g/L)	Ethanol (g/L)	corr'd** Ethanol (g/L)	GC Sugar Profile Arabinose (g/L)	Xylose (g/L)	Mannose (g/L)	Glucose (g/L)	Galactose (g/L)
0	1.26	0.10		2.11		2.47	6.78	16.32	40.46	3.63
1.8	2.19	0.34		2.50	0.39	2.54	6.49	16.19	38.18	2.75
3.75	2.91	0.46		2.83	0.72	2.53	6.94	14.83	35.69	2.85
8.5	7.88	0.90		7.51	5.40	2.36	6.80	13.64	23.32	2.76
17.2	14.98	1.18		15.95	13.84	2.06	6.58	10.59	6.37	3.75
19	15.18	1.18		18.37	16.26	1.76	6.24	9.23	2.95	3.26
21	16.88	1.23		17.97	15.85	2.27	6.74	8.19	1.85	3.19
22.9	18.38	1.26		18.26	16.14	2.12	6.76	7.31	0.82	2.99
24	17.68	1.25		18.31	16.20	1.97	5.52	6.86	0.80	3.49
26	19.18	1.28		18.66	16.55	1.96	5.23	4.96	0.40	2.91
27.4	19.98	1.30		18.77	16.66	2.12	5.59	4.39	0.00	3.33
29	20.48	1.31		19.12	17.01	2.09	5.18	3.63	0.00	3.31
32.3	21.78	1.34		18.89	16.78	2.04	4.96	2.26	0.00	3.02
41.8	22.58	1.35		16.93	14.82	2.07	4.63	0.00	0.00	3.10
45				16.99	14.88	1.91	4.25	0.00	0.00	2.79
50.5				16.53	14.42	1.68	4.27	0.00	0.00	2.78
66				13.36	11.25	1.56	3.58	0.00	0.00	1.02

Ferment'l Sugars (g/L)	Sugar Used (g/L)	Yield (EtOH/ Sugar) (g/g)
56.78		
54.37	2.41	0.16
50.52	6.26	0.12
36.96	19.82	0.27
16.96	39.82	0.35
12.18	44.6	0.36
10.04	46.74	0.34
8.13	48.65	0.33
7.66	49.12	0.33
5.36	51.42	0.32
4.39	52.39	0.32
3.63	53.15	0.32
2.26	54.52	0.31
0	56.78	0.26
0	56.78	0.26
0	56.78	0.25
0	56.78	0.20

Based on points, 3.75 --> 19 hr

Rate of Sugar Use (g/L/hr)	Rate of Alcohol Prod'n (g/L/hr)	Yp/s
2.47	1.00	0.40

* Note: ODs were measured on samples that had been frozen, and then thawed.

** Corr'd ethanol conc'n is the measured EtOH less that which existed at T=0

APPENDIX D

HYDROLYSIS SEPARATION DATA AND STATISTICAL ANALYSIS

Appendix B

Table B.1

Complete Table of SEDF Solid/Liquid Separation Data

Run No.	Pass No.	MEASURED VARIABLES Overs Flow (lb/min)	Overs Flow (kg/min)	% DS FEED	% DS OVERS	% DS UNDERS	%SUSP.SOL. FEED	%SUSP.SOL. OVERS	Glu Conc'n OVERS (g/L)	CALCULATED VARIABLES FEED Flow (kg/min)	UNDERS (kg/min)	% Sugar Recovery	% SUSP.SOL. UNDERS	% SUSP.SOL. Rec. in UNDERS	S.SOL. LOAD (g/min)	Comments	Stat. Name
SEP-A	1	11.8	5.3	14.6	10.1	29.5	11.4	6.2	36.0	7.0	1.6	80.7	28.4	58.5	792	HI DS, LO T, HI FLOW	ab
SEP-B	1	5.0	2.3	14.6	7.1	28.1	11.4	3.2	36.0	3.5	1.3	69.9	26.0	81.7	402	HI DS, LO T, LO FLOW	a
SEP-C	1	13.4	6.1	14.6	9.3	29.3	11.4	5.1	37.2	8.3	2.2	78.0	28.8	67.1	945	HI DS, HI T, HI FLOW	abc
SEP-D	1	6.8	3.1	14.6	6.2	28.3	11.4	2.2	37.2	4.9	1.9	68.0	26.3	87.9	563	HI DS, HI T, LO FLOW	ac
SEP-E	1	14.8	6.7	10.5	2.6	27.2			27.0	9.9	3.2	73.9				LO DS, HI T, LO FLOW	
SEP-F	1	14.6	6.6	14.0	10.5	25.7	9.5	5.7	39.5	8.7	2.0	79.9	22.0	53.8	825	HI DS, LO T, HI FLOW, BEROCEL	abd
SEP-G	1	6.0	2.7	14.0	7.2	25.7	9.5	2.3	39.5	4.3	1.6	68.0	21.8	84.7	412	HI DS, LO T, LO FLOW, BEROCEL	ad
SEP-H	1	14.8	6.7	14.1	9.6	27.6	9.5	5.1	43.4	9.0	2.2	78.9	22.7	59.6	854	HI DS, HI T, HI FLOW, BEROCEL	abcd
SEP-I	1	7.0	3.2	14.1	6.1	28.2	9.5	1.6	43.4	5.0	1.8	69.8	23.6	89.5	474	HI DS, HI T, LO FLOW, BEROCEL	acd
SEP-J	1	10.1	4.6	8.8	3.2	25.4			30.0	6.1	1.5	79.4				LO DS, HI T, LO FLOW, BEROCEL	

Table D.1 (cont'd)

Run No.	Pass No.	MEASURED VARIABLES Overs Flow (lb/min)	Overs Flow (kg/min)	% DS FEED	% DS OVERS	% DS UNDERS	%SUSP.SOL. FEED	%SUSP.SOL. OVERS	Glu Conc'n OVERS (g/L)	CALCULATED VARIABLES FEED Flow (kg/min)	UNDERS (kg/min)	% Sugar Recovery	% SUSP.SOL. UNDERS	% SUSP.SOL. in UNDERS	S.SOL. LOAD (g/min)	Comments	Stat. Name
SEP-K	1	17.9	8.1	7.8	4.5	26.1	5.5	2.1	22.0	9.6	1.5	87.7	24.0	67.6	524	LO DS, LO T, HI FLOW	b
SEP-L	1	10.1	4.6	7.8	4.0	25.0	5.5	1.6	21.5	5.6	1.0	85.0	22.6	76.1	307	LO DS, LO T, LO FLOW	(1)
SEP-M	1	18.1	8.2	8.0	4.0	26.1	5.5	1.6	22.0	10.0	1.8	85.8	23.4	76.0	545	LO DS, HI T, HI FLOW	bc
SEP-N	1	10.2	4.6	8.0	2.4	25.5	5.5	0.0	22.0	6.1	1.5	80.4	22.5	99.8	333	LO DS, HI T, LO FLOW	c
SEP-O	1	12.5	5.7	5.6	2.5	23.4			23.0	6.7	1.0	87.7				LO DS, HI T, LO FLOW	
SEP-P	1	15.3	6.9	10.4	6.6	25.7	7.6	3.7	24.1	8.6	1.7	83.8	23.9	61.2	657	LO DS, LO T, HI FLOW, BEROCEL	bd
SEP-Q	1	7.8	3.5	10.4	4.1	25.4	7.6	1.2	24.1	5.0	1.5	75.6	23.0	88.6	380	LO DS, LO T, LO FLOW, BEROCEL	d
SEP-R	1	16.6	7.5	10.4	5.8	28.0	7.6	2.6	23.0	9.5	2.0	83.2	26.5	72.6	728	LO DS, HI T, HI FLOW, BEROCEL	bcd
SEP-S	1	8.4	3.8	10.4	3.7	27.4	7.6	0.0	23.0	5.3	1.5	77.1	27.0	99.9	408	LO DS, HI T, LO FLOW, BEROCEL	cd
SEP-T	1	12.1	5.5	6.6	3.7	24.6			25.0	6.4	0.9	88.7				LO DS, HI T, LO FLOW, BEROCEL	

Appendix D

Table D.2

Contrast Matrix for 2^4 Factorial Experiment

Separation Expts. (SEDF) -- Effect of Feed DS (a), Feed Flow(b), Feed Temp(c), Berocell(d) on Sugar Recovery in Overs
N.B. Assumes no 3-factor or 4-factor interactions

No. of Replications= 1

Experiment Number	Treatment Combination	Treatment Total	(1)	(2)	(3)	(4)	Sum of Squares
L	(1)	85.0	154.9	323.3	635.5	1251.8	
B	a	69.9	168.4	312.2	616.3	-65.4	267.32
K	b	87.7	148.4	307.3	-42.3	64.2	257.60
A	ab	80.7	163.8	309.0	-23.1	19.4	23.52
N	c	80.4	143.6	-22.1	28.9	-9.4	5.52
D	ac	68.0	163.7	-20.2	35.3	1.8	0.20
M	bc	85.8	146.9	-11.5	12.7	-3.0	0.56
C	abc	78.0	162.1	-11.6	6.7	-4.2	1.10
Q	d	75.6	-15.1	13.5	-11.1	-19.2	23.04
G	ad	68.0	-7.0	15.4	1.7	19.2	23.04
P	bd	83.8	-12.4	20.1	1.9	6.4	2.56
F	abd	79.9	-7.8	15.2	-0.1	-6.0	2.25
S	cd	77.1	-7.6	8.1	1.9	12.8	10.24
I	acd	69.8	-3.9	4.6	-4.9	-2.0	0.25
R	bcd	83.2	-7.3	3.7	-3.5	-6.8	2.89
H	abcd	78.9	-4.3	3.0	-0.7	2.8	0.49

Table D.2 (cont'd)

Analysis of Variance Table

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Theoretical f
Main Effect					
A	267.32	1	267.32	191.42	6.61 (5% level)
B	257.60	1	257.60	184.46	16.26 (1% level)
C	5.52	1	5.52	3.95	
D	23.04	1	23.04	16.50	
2-Factor					
AB	23.52	1	23.52	16.84	
AC	0.20	1	0.20	0.15	
AD	23.04	1	23.04	16.50	
BC	0.56	1	0.56	0.40	
BD	2.56	1	2.56	1.83	
CD	10.24	1	10.24	7.33	
3-Factor					
ABC	1.10	0	ERR	ERR	
ABD	2.25	0	ERR	ERR	
ACD	0.25	0	ERR	ERR	
BCD	2.89	0	ERR	ERR	
4-Factor					
ABCD	0.49	0	ERR	ERR	
Error	6.98	5	1.40		
Total	620.60	15			

Appendix D

Table D.3

Contrast Matrix for 2^4 Factorial Experiment

Separation Expts. (SEDF) -- Effect of Feed DS (a), Feed Flow(b), Feed Temp(c), Berocell(d) on Recovery of Suspended Solids in Unders
N.B. Assumes no 3-factor or 4-factor interactions

No. of Replications= 1

Experiment Number	Treatment Combination	Treatment Total	(1)	(2)	(3)	(4)	Sum of Squares
L	(1)	76.1	157.8	283.9	614.7	1224.6	
B	a	81.7	126.1	330.8	609.9	-59.0	217.56
K	b	67.6	187.7	288.3	-24.3	-191.8	2299.20
A	ab	58.5	143.1	321.6	-34.7	-17.8	19.80
N	c	99.8	173.3	-3.5	-76.3	80.2	402.00
D	ac	87.9	115.0	-20.8	-115.5	-29.4	54.02
M	bc	76.0	189.4	-11.3	-11.7	-11.8	8.70
C	abc	67.1	132.2	-23.4	-6.1	18.6	21.62
Q	d	88.6	5.6	-31.7	46.9	-4.8	1.44
G	ad	84.7	-9.1	-44.6	33.3	-10.4	6.76
P	bd	61.2	-11.9	-58.3	-17.3	-39.2	96.04
F	abd	53.8	-8.9	-57.2	-12.1	5.6	1.96
S	cd	99.9	-3.9	-14.7	-12.9	-13.6	11.56
I	acd	89.5	-7.4	3.0	1.1	5.2	1.69
R	bcd	72.6	-10.4	-3.5	17.7	14.0	12.25
H	abcd	59.6	-13.0	-2.6	0.9	-16.8	17.64

Table D.3 (cont'd)

Analysis of Variance Table

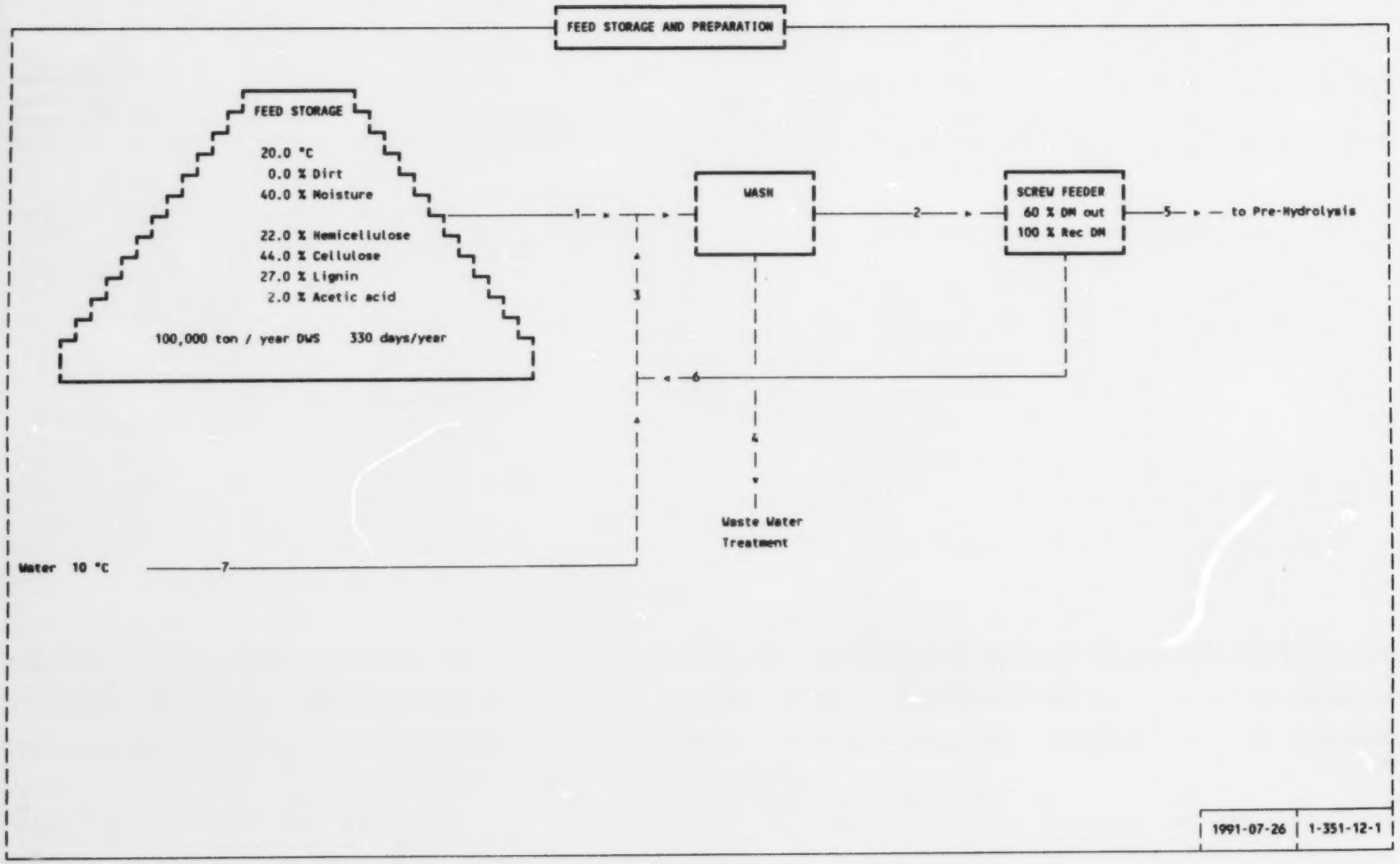
Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Theoretical f
Main Effect					
A	217.56	1	217.56	19.72	6.61 (5% level)
B	2299.20	1	2299.20	208.40	16.26 (1% level)
C	402.00	1	402.00	36.44	
D	1.44	1	1.44	0.13	
2-Factor					
AB	19.80	1	19.80	1.79	
AC	54.02	1	54.02	4.90	
AD	6.76	1	6.76	0.61	
BC	8.70	1	8.70	0.79	
BD	96.04	1	96.04	8.71	
CD	11.56	1	11.56	1.05	
3-Factor					
ABC	21.62	0	ERR	ERR	
ABD	1.96	0	ERR	ERR	
ACD	1.69	0	ERR	ERR	
BCD	12.25	0	ERR	ERR	
4-Factor					
ABCD	17.64	0	ERR	ERR	
Error	55.16	5	11.03		
Total	3172.26	15			

APPENDIX E

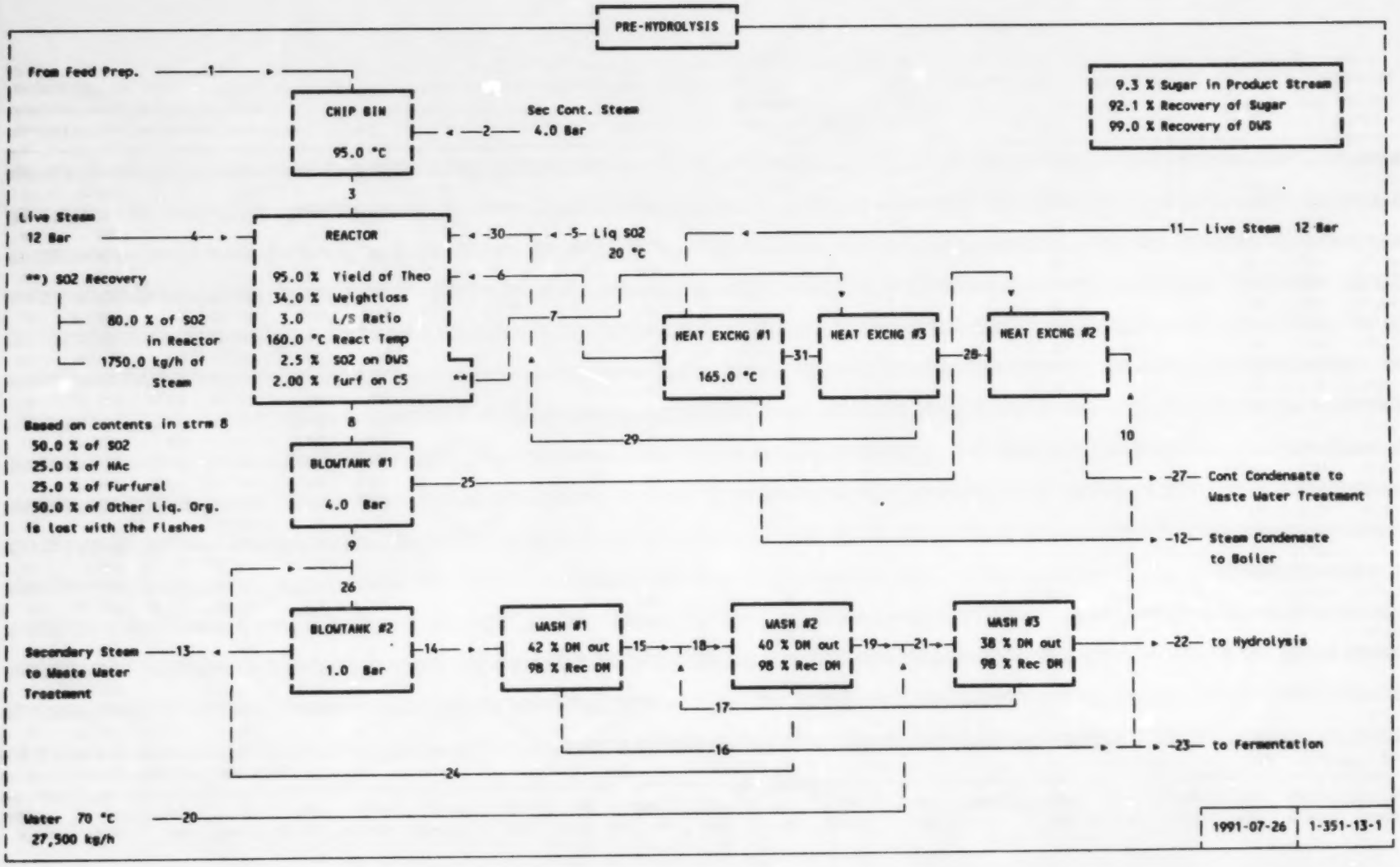
MASS BALANCE AND ECONOMIC DATA

E.1 "Stand-Alone" CASH Facility

- Mass Balance
- Wood Hydrolyis Cost Summary
- Wood Hydrolysis Process Area Summary
- Wood Hydrolysis Device List


FEED STORAGE AND PREPARATION
FEED STORAGE
20.0 °C
0.0 % Dirt
40.0 % Moisture
22.0 % Hemicellulose
44.0 % Cellulose
27.0 % Lignin
2.0 % Acetic acid
100,000 ton / year DWS 330 days/year
WASH
SCREW FEEDER
60 % DM out
100 % Rec DM
to Pre-Hydrolysis
Waste Water Treatment
Water 10 °C
1
2
3
4
5
6
7
1991-07-26
1-351-12-1

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
1	21,044	12,626	8,418															20	1.00	1,042
3																		20	1.00	
5	21,044	12,626	8,418															20	1.00	1,042
7																		10	1.00	

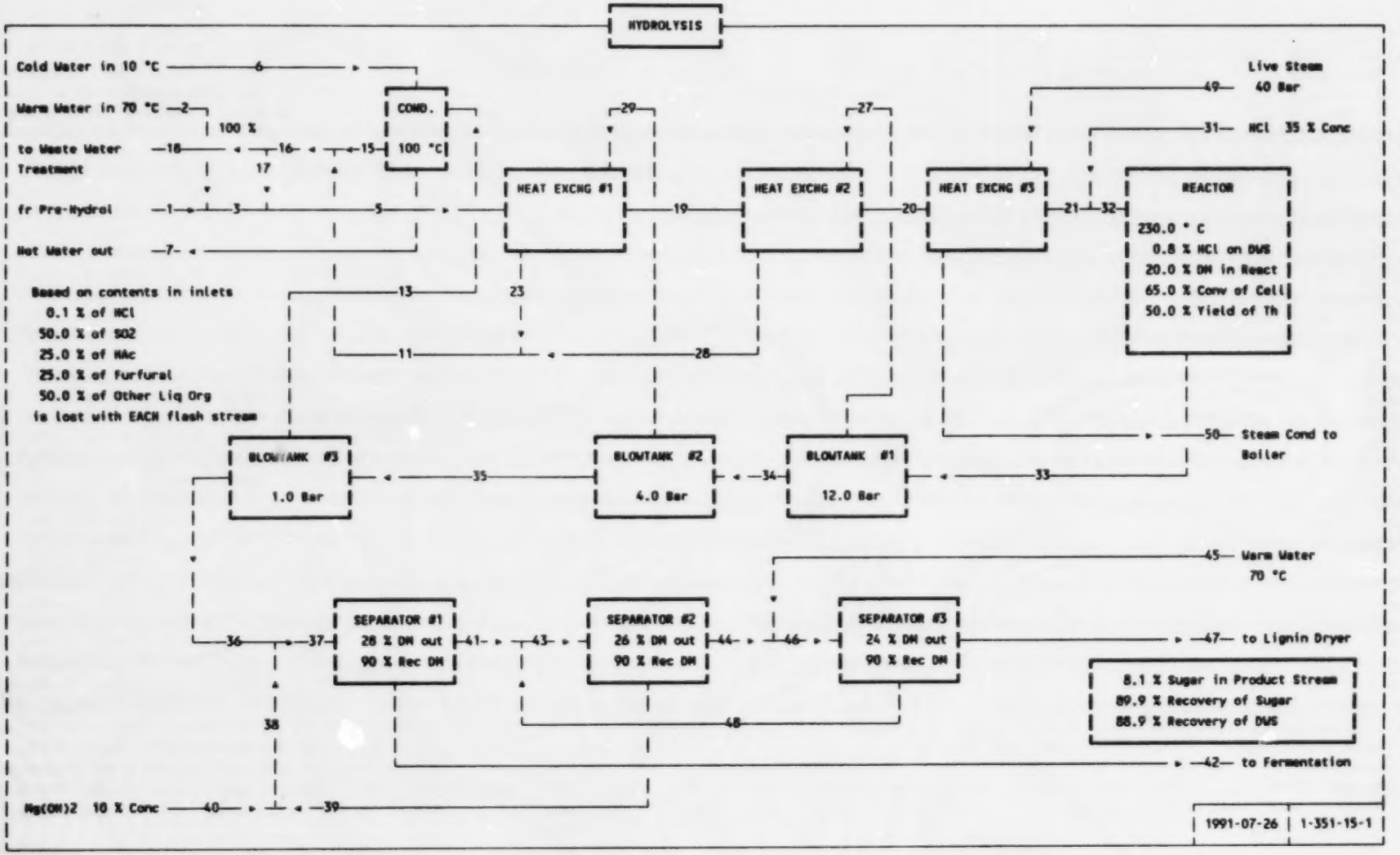

PRE-HYDROLYSIS
From Feed Prep.
1
CHIP BIN
95.0 °C
Sec Cont. Steam
4.0 Bar
2
3
9.3 % Sugar in Product Stream
92.1 % Recovery of Sugar
99.0 % Recovery of DWS
Live Steam
12 Bar
4
REACTOR
95.0 % Yield of Theo
34.0 % Weightloss
3.0 L/S Ratio
160.0 °C React Temp
2.5 % SO2 on DWS
2.00 % Furf on C5
**
-30
-5- Liq SO2
20 °C
11— Live Steam 12 Bar
6
7
HEAT EXCHG #1
165.0 °C
31
HEAT EXCHG #3
28
HEAT EXCHG #2
**) SO2 Recovery
80.0 % of SO2
in Reactor
1750.0 kg/h of
Steam
Based on contents in strm 8
50.0 % of SO2
25.0 % of HAc
25.0 % of Furfural
50.0 % of Other Liq. Org.
is lost with the Flashes
8
29
10
BLOWTANK #1
4.0 Bar
25
-27— Cont Condensate to
Waste Water Treatment
-12— Steam Condensate
to Boiler
9
26
BLOWTANK #2
1.0 Bar
Secondary Steam
13
to Waste Water
Treatment
14
WASH #1
42 % DM out
98 % Rec DM
15
18
WASH #2
40 % DM out
98 % Rec DM
19
21
WASH #3
38 % DM out
98 % Rec DM
-22— to Hydrolysis
17
16
-23— to Fermentation
24
Water 70 °C
27,500 kg/h
20
1991-07-26
1-351-13-1

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
1	21,044	12,626	8,418															20	1.00	1,042
3	22,713	12,626	10,087															95	1.00	5,614
5	56										56							20		1
7	2,003		1,750								253							139		4,804
9	50,783	8,421	36,129	1,132	4,003			23	787		32				256			144	4.00	24,471
11	1,549		1,549															188	12.00	4,316
13	3,054		2,519					7	436		17				75			100	1.00	6,811
15	23,863	8,421	13,840	318	1,125			5	99		4				51			100	1.00	7,096
17	27,935	168	27,315	90	318			1	28		1				14			76	1.00	8,687
19	22,746	8,418	13,648	135	478			2	42		2				22			85	1.00	5,846
21	50,246	8,418	41,148	135	478			2	42		2				22			76	1.00	13,912
23	25,884	84	23,125	532	1,880			8	165		7				85			100	1.00	9,985
25	912							8	787		32				85			144	4.00	173
27	912							8	787		32				85			144	4.00	173
29	2,003		1,750								253							139		1,038

Swedish Ethanol Development Foundation
Mass and Energy Calculation Report
BALANCE.EXE Ver 1.22

PRE-HYDROLYSIS

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
31	27,036	88	24,154	555	1,963			8	172		7				89			136	1.00	14,195


HYDROLYSIS
Cold Water in 10 °C
6
Warm Water in 70 °C
2
100 %
to Waste Water Treatment
18
16
15
17
COND.
100 °C
fr Pre-Hydrol
1
3
5
Hot Water out
7
Based on contents in inlets
0.1 % of HCl
50.0 % of SO2
25.0 % of HAc
25.0 % of Furfural
50.0 % of Other Liq Org
is lost with EACH flash stream
HEAT EXCHG #1
HEAT EXCHG #2
HEAT EXCHG #3
29
27
19
20
21
32
13
23
11
28
Live Steam
49
40 Bar
31
HCl 35 % Conc
REACTOR
230.0 ° C
0.8 % HCl on DWS
20.0 % DM in React
65.0 % Conv of Cell
50.0 % Yield of Th
50
Steam Cond to Boiler
BLOWTANK #3
1.0 Bar
BLOWTANK #2
4.0 Bar
BLOWTANK #1
12.0 Bar
35
34
33
45
Warm Water 70 °C
SEPARATOR #1
28 % DM out
90 % Rec DM
SEPARATOR #2
26 % DM out
90 % Rec DM
SEPARATOR #3
24 % DM out
90 % Rec DM
36
37
41
43
44
46
47
to Lignin Dryer
8.1 % Sugar in Product Stream
89.9 % Recovery of Sugar
88.9 % Recovery of DWS
38
48
42
to Fermentation
Mg(OH)2 10 % Conc
40
39
1991-07-26
1-351-15-1

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
1	22,311	8,249	13,833	45	161			1	14		1				7			76	1.00	5,225
3	42,532	8,249	34,054	45	161			1	14		1				7			72	1.00	11,142
5	42,532	8,249	34,054	45	161			1	14		1				7			72	27.98	11,142
7	14,860		14,860															100		6,212
9																				
11	6,565		5,865					6	690						3			167		4,233
13	2,593		2,475					2	115						1			100	1.00	6,636
15	2,593		2,475					2	115						1			100	1.00	1,046
17																		147		
19	42,532	8,249	34,054	45	161			1	14		1				7			112	27.98	17,221
21	42,532	8,249	34,054	45	161			1	14		1				7			230	27.98	35,350
23	3,077		2,843					3	230						1			144	4.00	1,749
25																				
27	3,488		3,022					4	460						2			188	12.00	8,526
29	3,077		2,843					3	230						1			144	4.00	7,828

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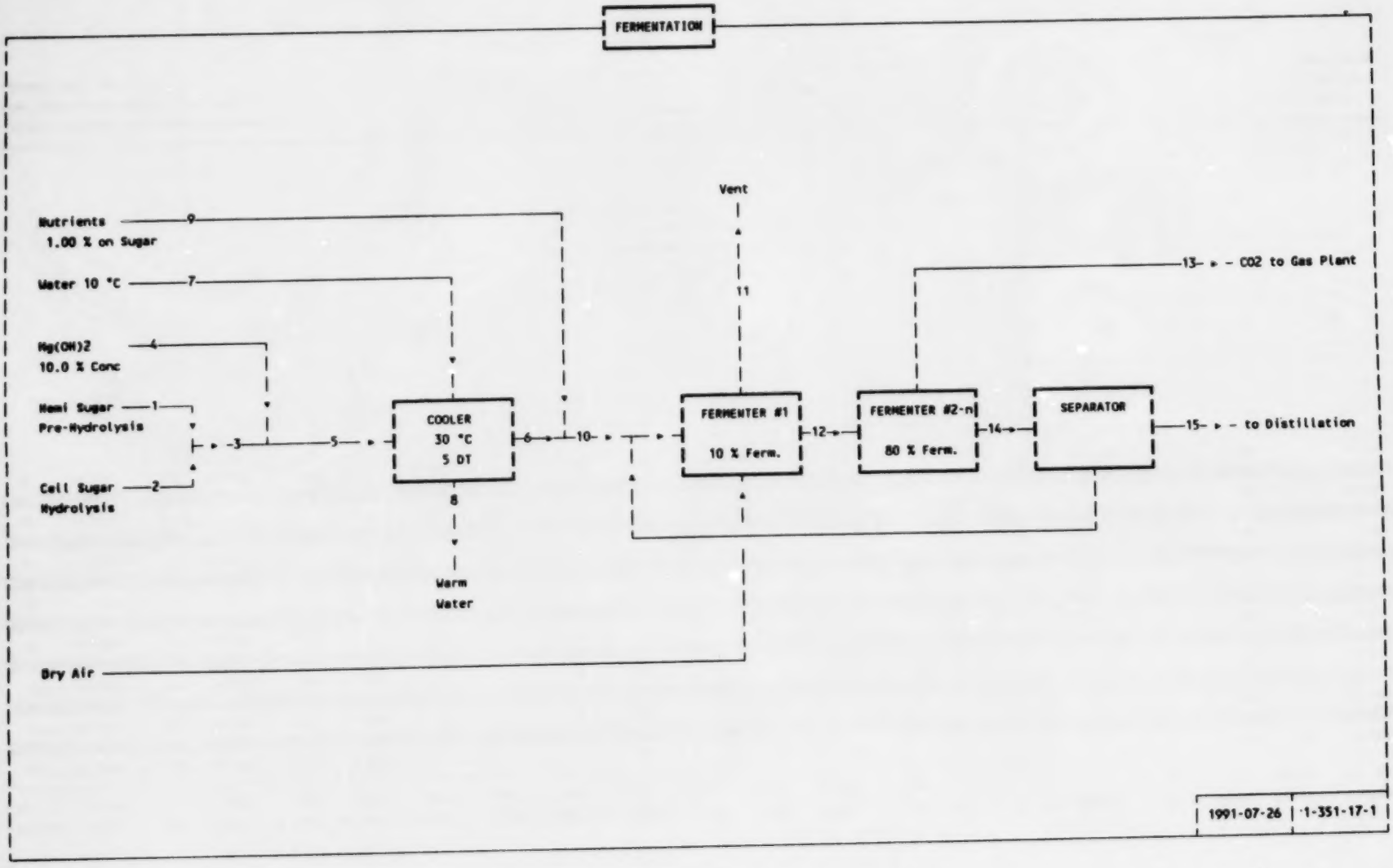
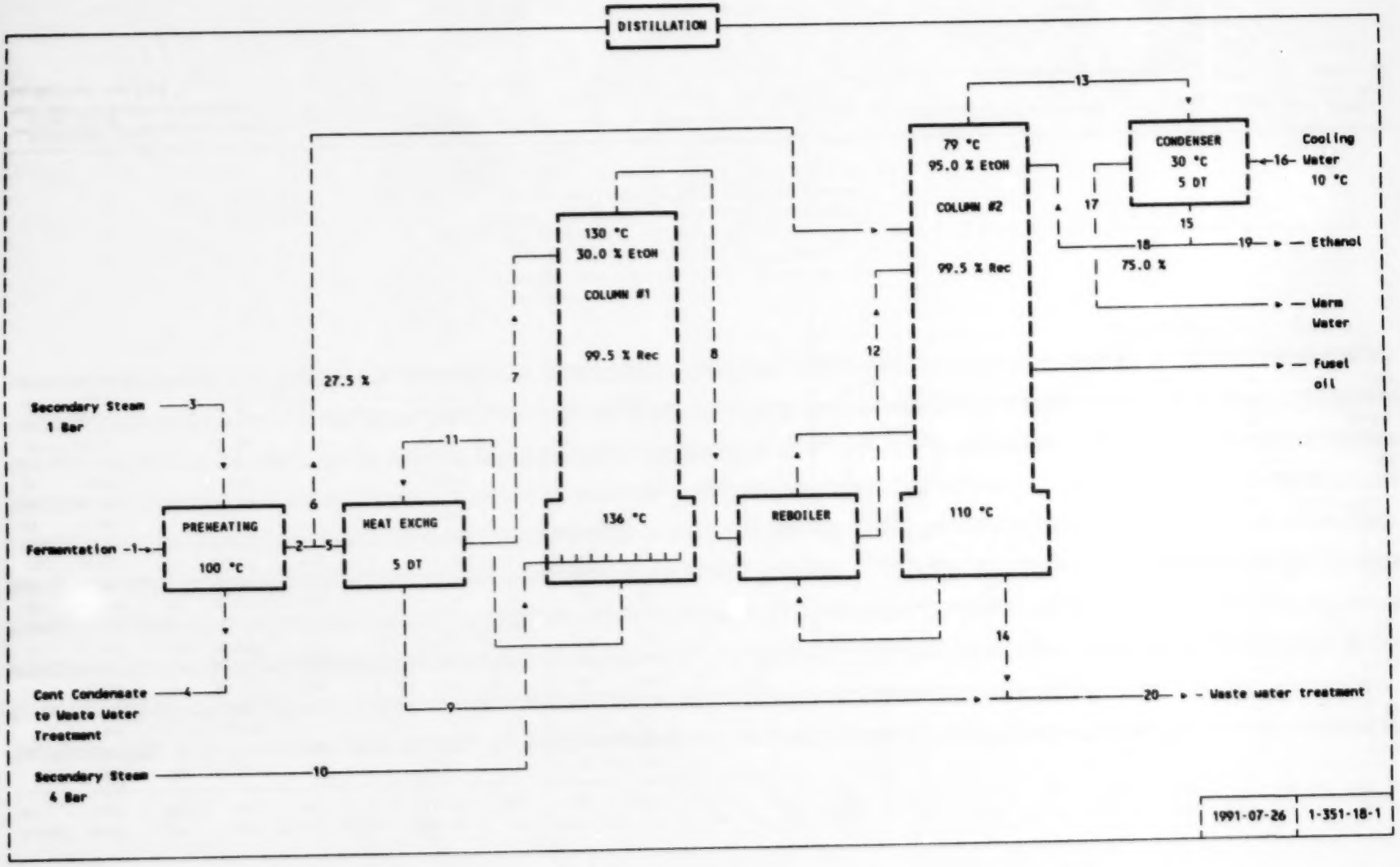
HYDROLYSIS

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
31	189		123										66					20		11
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]		[illegible]		[illegible]		[illegible]			[illegible]		[illegible]
33	42,721	4,675	33,874	32	3,133			14	919		1		66		7			230	27.98	35,210
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]				[illegible]		[illegible]			[illegible]		[illegible]
35	36,156	4,675	28,009	32	3,133			8	230				66		4			144	4.00	18,340
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]				[illegible]		[illegible]			[illegible]		[illegible]
37	57,331	5,188	47,581	43	4,234			8	155					116		5		93		19,601
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]				[illegible]		[illegible]		[illegible]		[illegible]
39	23,394	513	21,695	11	1,102			2	40					30		1		84		7,776
[illegible]	[illegible]		[illegible]							[illegible]										
41	22,131	4,669	15,934	14	1,418			3	52					39		2		93		6,928
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]					[illegible]		[illegible]		[illegible]		[illegible]
43	44,430	5,131	37,261	19	1,892			4	69					52		2		84		13,833
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]					[illegible]		[illegible]		[illegible]		[illegible]
45	20,000		20,000															70	1.00	5,852
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]					[illegible]		[illegible]		[illegible]		[illegible]
47	18,737	4,156	14,240	3	316			1	12					9				76		5,004
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]					[illegible]		[illegible]		[illegible]		[illegible]
49	7,055		7,055															250	40.00	19,759
[illegible]	[illegible]		[illegible]															[illegible]		[illegible]


FERMENTATION
Vent
Nutrients
1.00 % on Sugar
9
Water 10 °C
7
11
13 - CO2 to Gas Plant
Mg(OH)2
10.0 % Conc
4
Hemi Sugar
Pre-Hydrolysis
1
Cell Sugar
Hydrolysis
2
3
5
COOLER
30 °C
5 DT
6
10
FERMENTER #1
10 % Ferm.
12
FERMENTER #2-n
80 % Ferm.
14
SEPARATOR
15 - to Distillation
8
Warm
Water
Dry Air
1991-07-26
1-351-17-1

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
1	25,884	84	23,125	532	1,880			8	165		7				85			100	1.00	9,985
3	61,084	603	54,772	560	4,696			13	268		7			77	85	3		96		22,658
5	61,409	603	55,077	560	4,696			13	268			11		77		104		96		22,658
7	46,030		46,030															10		1,924
9	53								53											
11	230						230											30		5,648
13	1,837						1,837											30		45,182
15	59,395	603	55,077	560		2,160		13	790			11		77		104		30		7,148


DISTILLATION
79 °C
95.0 % EtOH
COLUMN #2
99.5 % Rec
CONDENSER
30 °C
5 DT
Cooling
Water
10 °C
16
17
15
18
19
Ethanol
75.0 %
Warm
Water
Fusel
oil
13
130 °C
30.0 % EtOH
COLUMN #1
99.5 % Rec
136 °C
27.5 %
7
8
12
11
Secondary Steam
1 Bar
3
PREHEATING
100 °C
HEAT EXCHG
5 DT
REBOILER
110 °C
Fermentation
1
2
5
6
14
Cont Condensate
to Waste Water
Treatment
4
9
20
Waste water treatment
Secondary Steam
4 Bar
10
1991-07-26
1-351-18-1

Stream No	Total kg/h	DWS kg/h	Water kg/h	CS Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
1	59,395	603	55,077	560		2,160		13	790			11		77		104		30		7,148
2	59,395	603	55,077	560		2,160		13	790			11		77		104		100		19,764
3	7,388		7,388															100	1.00	19,764
4	7,388		7,388															100	1.00	19,764
5	43,038	437	39,909	406		1,565		10	573			8		56		75		100		17,265
6	16,357	166	15,168	154		595		4	218			3		21		29		100		17,265
7	43,038	437	39,909	406		1,565		10	573			8		56		75		131		22,624
8	5,191		3,634			1,557												131		22,624
9	42,439	437	40,867	406		8		10	573			8		56		75		105		18,152
10	4,590		4,592															105	1.00	18,152
11	42,439	437	40,867	406		8		10	573			8		56		75		136		23,511
12	5,191		3,634			1,557												136		23,511
13	9,017		451			8,566												79		10,079
14	19,296	166	18,689	154		11		4	218			3		21		29		110		3,481
15	9,017		451			8,566												30		681
16	35,129		35,129															30		681
17	35,129		35,129															74		10,866
18	6,765		338			6,425												30		511
19	2,254		113			2,142												30		170
20	61,733	603	59,556	560		19		13	790			11		77		104		107		28,653

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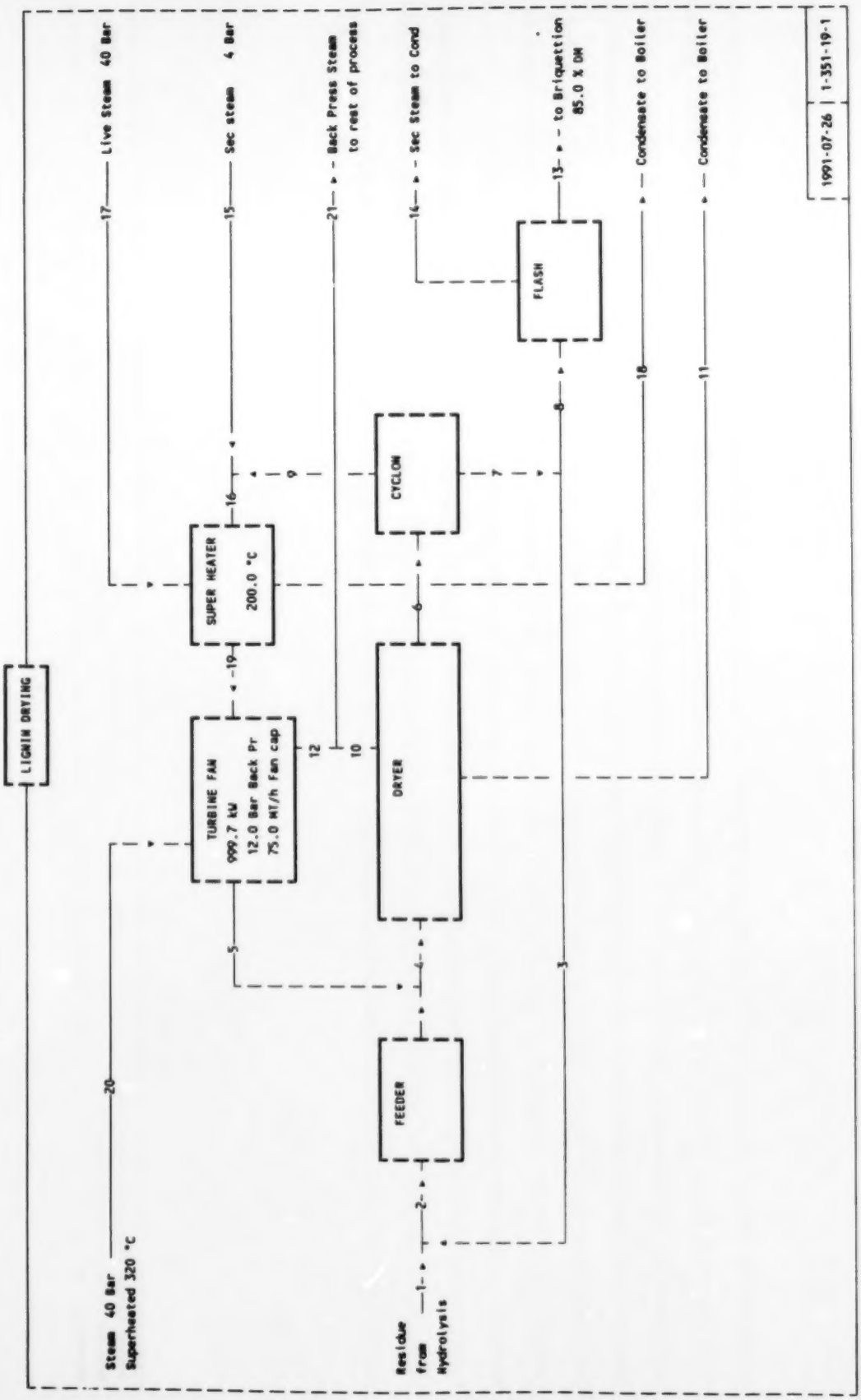
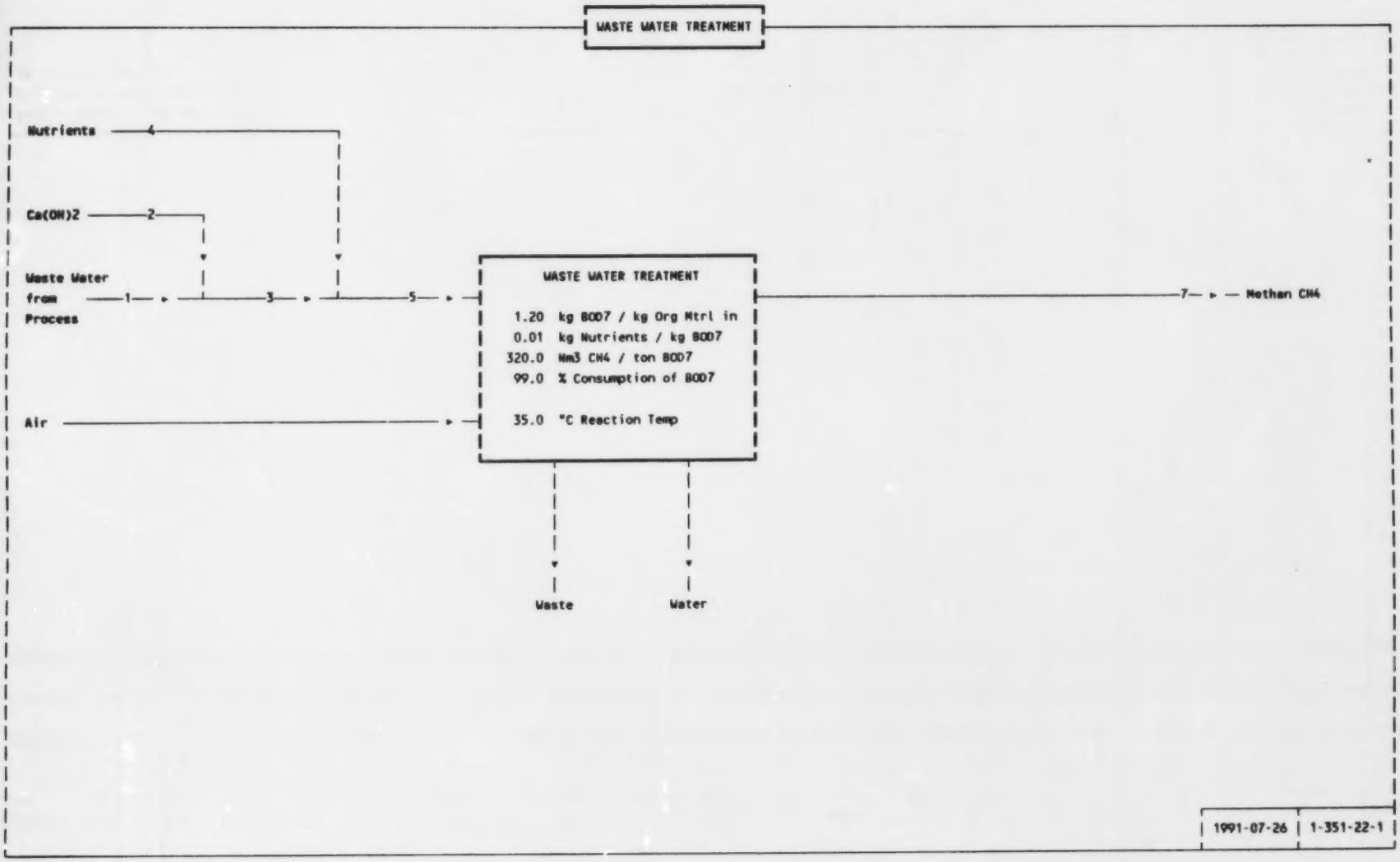
DISTILLATION


LIGNIN DRYING
Steam 40 Bar
Superheated 320 °C
Residue
from
Hydrolysis
FEEDER
TURBINE FAN
999.7 kW
12.0 Bar Back Pr
75.0 MT/h Fan cap
SUPER HEATER
200.0 °C
DRYER
CYCLON
FLASH
Live Steam 40 Bar
Sec steam 4 Bar
Back Press Steam
to rest of process
Sec Steam to Cond
to Briquettion
85.0 % DM
Condensate to Boiler
Condensate to Boiler
1991-07-26 | 1-351-19-1

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
1	18,737	4,156	14,240	3	316			1	12					9				76		5,004
2	21,088	5,937	14,664	5	452			1	17					12		1		51		1,337
3	2,351	1,781	424	1	136				5					4				144	4.00	624
4	94,664	5,937	89,664	5	452			1	17					12		1		116		30,963
5	75,000		75,000															200	4.00	214,320
6	89,664	5,937	89,664	5	452			1	17					12		1		144	4.00	2,079
7	7,837	5,937	1,413	5	452			1	17					12		1		144	4.00	2,079
8	5,086	4,156	929	3	316			1	12					9				144	4.00	241,688
9	88,250		88,250															188	12.00	35,375
10	11,992		11,992															188	12.00	9,575
11	11,992		11,992															188	12.00	9,575
12	15,430		15,430															100	1.00	931
13	5,290	4,156	794	3	316			1	12					9				100	1.00	376
14	196		196															144	4.00	36,289
15	13,250		13,250															144	4.00	705,000
16	75,000		75,000															250	40.00	14,582
17	5,206		5,206															250	40.00	1,445
18	5,206		5,206															200	4.00	214,320
19	75,000		75,000															320	40.00	35,565
20	15,430		15,430															188	12.00	9,571
21	3,437		3,437																	


WASTE WATER TREATMENT
Nutrients
4
Ca(OH)2
2
Waste Water
from
Process
1
3
5
WASTE WATER TREATMENT
1.20 kg BOD7 / kg Org Mtrl in
0.01 kg Nutrients / kg BOD7
320.0 Nm3 CH4 / ton BOD7
99.0 % Consumption of BOD7
35.0 °C Reaction Temp
Air
7
Methan CH4
Waste
Water
1991-07-26
1-351-22-1

Stream No	Total kg/h	DWS kg/h	Water kg/h	C5 Sug. kg/h	C6 Sug. kg/h	Ethanol kg/h	CO2 kg/h	Furf. kg/h	Liq. org kg/h	MgO kg/h	SO2 kg/h	MgSO3 kg/h	HCl kg/h	MgCl2 kg/h	HAc kg/h	Mg(Ac)2 kg/h	Dirt kg/h	Temp. °C	Press. Bar(a)	Energy 0°C MJ
1	75,051	603	70,610	560		19		36	2,817		50	11		77	164	104		35		10,534
3	75,228	603	70,638	560		19		36	2,817			104		77		373		35		10,534
5	75,272	603	70,638	560		19		36	2,862			104		77		373		35		10,534
7	1,185						1,185													

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WASTE WATER TREATMENT

Page: 1
1-351-22-1
1991-07-26

SEDF / 91-07-29 **WOODHYDROLYSIS COST SUMMARY** 1/3

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

		SEK kKR
Production costs	: See page 3	46,132
Production credits	: See page 3	-30,650
Production overhead	: See page 3	21,500
ANNUAL PRODUCTION COST		36,982
ANNUAL CAPITAL COSTS	: See page 2	77,754
TOTAL ANNUAL COST		114,737

ANNUAL COST **5.14 SEK/l Ethanol**

SEDF / 91-07-29 **WOODHYDROLYSIS CAPITAL COSTS** 2/3

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.

CAPITAL COSTS : @ 100,000 ton/year DWS in feedstock		SEK kKR
FEED STORAGE	Purchase	10,275
	Erection +Eng	6,340
PRE-HYDROLYSIS REACTOR AND BLOW DOWN	Purchase	14,734
	Erection +Eng	14,723
PRE-HYDROLYSIS WASH AND SEPARATION	Purchase	17,700
	Erection +Eng	12,472
HYDROLYSIS REACTOR AND BLOW DOWN	Purchase	12,874
	Erection +Eng	16,960
HYDROLYSIS WASH AND SEPARATION	Purchase	13,594
	Erection +Eng	18,651
FERMENTATION	Purchase	7,079
	Erection +Eng	16,268
ETHANOL DESTILLATION	Purchase	10,068
	Erection +Eng	11,117
LIGNIN DRYER	Purchase	31,859
	Erection +Eng	11,639
BRIQUETTING	Purchase	4,419
	Erection +Eng	5,971
STEAM BOILER PLANT HIGH PRESSURE	Purchase	21,284
	Erection +Eng	21,123
WASTE WATER TREATMENT PLANT	Purchase	21,904
	Erection +Eng	12,293
PLANT- AND INSTRUMENT AIR SUPPLY	Purchase	3,967
	Erection +Eng	10,350
STEAM BOILER PLANT LOW PRESSURE	Purchase	12,284
	Erection +Eng	21,123
ELECTRICAL AND INSTRUMENT CENTRE	Purchase	1,435
	Erection +Eng	4,965
		367,465
Ratio feedstock 1.00 Raised to the power of 0.70		
SUBTOTAL		367,465
Contingency	15 %	55,120
Interest / construction	10 %	36,747
TOTAL		459,332
Capital cost/year	10 % interest and 10 year write off	74,754
Working capital	10 % of 30,000	3,000
GRAND TOTAL		77,754

ANNUAL CAPITAL COST **3.48 SEK/l Ethanol**

SEDF / 91-07-29 **WOODHYDROLYSIS PRODUCTION COSTS** 3/3

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.

PRODUCTION COSTS :						SEK kKR
Pine Saw Dust	100,000	ton/year	a'	220	SEK/ton	22,000
Energy steam	640,780	GJ/year	a'	21	SEK/GJ	13,456
Power 60% of	37,738	MWh/year	a'	275	SEK/MWh	6,227
SO2	445	ton/year	a'	1,430	SEK/ton	637
HCl	523	ton/year	a'	1,320	SEK/ton	690
MgO	552	ton/year	a'	1,700	SEK/ton	939
CaO	959	ton/year	a'	1,080	SEK/ton	1,035
Nutrients Ferm	416	ton/year	a'	1,500	SEK/ton	624
Nutrients Waste	349	ton/year	a'	1,500	SEK/ton	524
Water	1,810,932	ton/year	a'	0.00	SEK/ton	
SUM						46,132

PRODUCTION CREDITS :						
Condensate	188,940	GJ/year	a'	21	SEK/GJ	-3,968
Lignin DWS	32,914	ton/year	a'	506	SEK/ton	-16,655
CO2	14,546	ton/year	a'	12	SEK/ton	-175
Methan	469,184	GJ/year	a'	21	SEK/GJ	-9,853
SUM						-30,650

Labour, Management, Repair, Maintenance and Insurance	21,500
GRAND TOTAL	36,982

ANNUAL PRODUCTION COST **1.66 SEK/l Ethanol**

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

PROCESS AREA #11 FEED STORAGE

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	9,720,000		77	9,720,000
Piping CS/SS	25,000	25,000		80,000
Valves Manual	30,000			
Control				
Instrument	150,000	75,000		225,000
Electrical	350,000	900,000		1,250,000
Construction		3,000,000		3,000,000
Insulation				
Engineering		1,625,000		
travells		525,000		
rent etc		190,000		2,340,000
SUB TOTAL	10,275,000	6,340,000	77	16,615,000
Feed ratio 1.00 and power factor 0.70				
GRAND TOTAL				16,615,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #13 PRE-HYDROLYSIS REACTOR AND BLOW DOWN

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	13,710,000	67,500	830	13,777,500
Piping CS/SS	192,250	170,500		564,750
Valves Manual	131,000			
Control	71,000			
Instrument	300,000	150,000		450,000
Electrical	330,000	150,000		480,000
Construction		12,310,000		12,310,000
Insulation		205,000		205,000
Engineering		835,000		
travells		750,000		
rent etc		85,000		1,670,000
SUB TOTAL	14,734,250	14,723,000	830	29,457,250

Feed ratio 1.00 and power factor 0.70

GRAND TOTAL 29,457,250

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #14 PRE-HYDROLYSIS WASH AND SEPARATION

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	16,620,000	14,500	505	16,634,500
Piping CS/SS	152,500	152,500		572,000
Valves Manual	134,000			
Control	133,000			
Instrument	450,000	225,000		675,000
Electrical	210,000	300,000		510,000
Construction		8,600,000		8,600,000
Insulation		220,000		220,000
Engineering		1,845,000		
travells		750,000		
rent etc		365,000		2,960,000
SUB TOTAL	17,699,500	12,472,000	505	30,171,500
Feed ratio 1.00 and power factor 0.70				
GRAND TOTAL				30,171,500

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #15 HYDROLYSIS REACTOR AND BLOW DOWN

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	12,080,000	14,500	210	12,094,500
Piping CS/SS	130,250	115,250		419,500
Valves Manual	108,000			
Control	66,000			
Instrument	300,000	150,000		450,000
Electrical	190,000	150,000		340,000
Construction		12,700,000		12,700,000
Insulation		255,000		255,000
Engineering		2,460,000		
travells		750,000		
rent etc		365,000		3,575,000
SUB TOTAL	12,874,250	16,959,750	210	29,834,000
Feed ratio 1.00 and power factor 0.70				
GRAND TOTAL				29,834,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

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PROCESS AREA #16 HYDROLYSIS WASH AND SEPARATION

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	12,370,000	18,000	691	12,388,000
Piping CS/SS	232,500	232,500		691,000
Valves Manual	175,000			
Control	51,000			
Instrument	450,000	225,000		675,000
Electrical	315,000	225,000		540,000
Construction		12,700,000		12,700,000
Insulation		310,000		310,000
Engineering		3,125,000		
travells		750,000		
rent etc		1,065,000		4,940,000

SUB TOTAL	13,593,500	18,650,500	691	32,244,000
Feed ratio 1.00	and power factor 0.70			
GRAND TOTAL				32,244,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #17 FERMENTATION

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	5,920,000	2,141,500	400	8,061,500
Piping CS/SS	121,000	121,000		485,000
Valves Manual	138,000			
Control	105,000			
Instrument	450,000	225,000		675,000
Electrical	345,000	225,000		570,000
Construction		9,000,000		9,000,000
Insulation		490,000		490,000
Engineering		2,600,000		
travells		750,000		
rent etc		715,000		4,065,000

SUB TOTAL	7,079,000	16,267,500	400	23,346,500
Feed ratio 1.00	and power factor 0.70			
GRAND TOTAL				23,346,500

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #18 ETHANOL DESTILLATION

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	8,500,000	1,270,000	110	9,770,000
Piping CS/SS	242,000	242,000		900,000
Valves Manual	230,000			
Control	186,000			
Instrument	660,000	330,000		990,000
Electrical	250,000	150,000		400,000
Construction		5,000,000		5,000,000
Insulation		285,000		285,000
Engineering		2,375,000		
travells		750,000		
rent etc		715,000		3,840,000
SUB TOTAL	10,068,000	11,117,000	110	21,185,000
Feed ratio 1.00 and power factor 0.70				
GRAND TOTAL				21,185,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #19 LIGNIN DRYER

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	30,000,000	2,000,000	320	32,000,000
Piping CS/SS	1,018,750	1,018,750		2,367,500
Valves Manual	240,000			
Control	90,000			
Instrument	300,000	150,000		450,000
Electrical	210,000	150,000		360,000
Construction		4,500,000		4,500,000
Insulation		175,000		175,000
Engineering		2,180,000		
travells		750,000		
rent etc		715,000		3,645,000

SUB TOTAL	31,858,750	11,638,750	320	43,497,500
Feed ratio	1.00 and power factor	0.70		
GRAND TOTAL				43,497,500

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

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PROCESS AREA #20 BRIQUETTING

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	4,000,000	200,000	100	4,200,000
Piping CS/SS	68,750	68,750		277,500
Valves Manual	140,000			
Control				
Instrument				
Electrical	210,000	150,000		360,000
Construction		4,310,000		4,310,000
Insulation				
Engineering		685,000		
travells		525,000		
rent etc		32,500		1,242,500

SUB TOTAL	4,418,750	5,971,250	100	10,390,000
Feed ratio 1.00	and power factor 0.70			
GRAND TOTAL				10,390,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #21 STEAM BOILER PLANT HIGH PRESSURE

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	19,000,000	2,000,000	250	21,000,000
Piping CS/SS	857,500	857,500		2,321,000
Valves Manual	386,000			
Control	220,000			
Instrument	600,000	300,000		900,000
Electrical	220,000	300,000		520,000
Construction		12,800,000		12,800,000
Insulation		150,000		150,000
Engineering		2,900,000		
travells		750,000		
rent etc		1,065,000		4,715,000
SUB TOTAL	21,283,500	21,122,500	250	42,406,000
Feed ratio 1.00 and power factor 0.70				
GRAND TOTAL				42,406,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #22 WASTE WATER TREATMENT PLANT

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	20,000,000	5,000,000	355	25,000,000
Piping CS/SS	637,500	637,500		1,595,000
Valves Manual	170,000			
Control	150,000			
Instrument	300,000	150,000		450,000
Electrical	646,000	90,000		736,000
Construction		3,000,000		3,000,000
Insulation		100,000		100,000
Engineering		1,850,000		
travells		750,000		
rent etc		715,000		3,315,000
SUB TOTAL	21,903,500	12,292,500	355	34,196,000
Feed ratio 1.00 and power factor 0.70				
GRAND TOTAL				34,196,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #23 PLANT- AND INSTRUMENT AIR SUPPLY

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	3,000,000	25,000	260	3,025,000
Piping CS/SS	267,500	267,500		849,000
Valves Manual	210,000			
Control	104,000			
Instrument	300,000	150,000		450,000
Electrical	85,000	75,000		160,000
Construction		8,350,000		8,350,000
Insulation		67,500		67,500
Engineering		440,000		
travells		750,000		
rent etc		225,000		1,415,000

SUB TOTAL	3,966,500	10,350,000	260	14,316,500
Feed ratio 1.00	and power factor 0.70			
GRAND TOTAL				14,316,500

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

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PROCESS AREA #24 STEAM BOILER PLANT LOW PRESSURE

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	10,000,000	2,000,000	200	12,000,000
Piping CS/SS	857,500	857,500		2,321,000
Valves Manual	386,000			
Control	220,000			
Instrument	600,000	300,000		900,000
Electrical	220,000	300,000		520,000
Construction		12,800,000		12,800,000
Insulation		150,000		150,000
Engineering		2,900,000		
travells		750,000		
rent etc		1,065,000		4,715,000
SUB TOTAL	12,283,500	21,122,500	200	33,406,000

Feed ratio 1.00 and power factor 0.70

GRAND TOTAL 33,406,000

SEDF / 91-07-26 **WOODHYDROLYSIS PROCESS AREA SUMMARY**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

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PROCESS AREA #99 ELECTRICAL AND INSTRUMENT CENTRE

Prices @ 100,000 ton/year DM in feedstock

	Purchase SEK	Erection SEK	Power kW	Total SEK
Devices	1,300,000			1,300,000
Piping CS/SS				
Valves Manual				
Control				
Instrument				
Electrical	135,000	150,000		285,000
Construction				
Insulation				
Engineering		3,700,000		
travells		750,000		
rent etc		365,000		4,815,000
SUB TOTAL	1,435,000	4,965,000		6,400,000
Feed ratio 1.00	and power factor 0.70			
GRAND TOTAL				6,400,000

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

PROCESS AREA #11 FEED STORAGE

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
A 1101	Charge bin	1	20	2,300,000	
A 1102	Elevator / Conveyor	1	5	300,000	
A 1103	Top elevator	1	3	1,500,000	
A 1104	Stack feed screw	1	30		
A 1105	Stack Conveyor	1	3		
A 1106	Screen conveyor	1	3	100,000	
A 1107	Screen	1	5	500,000	
A 1108	Screen conveyor	1	3	20,000	
A 1109	Feed conveyor	1	5	2,500,000	
A 1199	A 1104 - A-1105	1		2,500,000	

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #13 PRE-HYDROLYSIS REACTOR AND BLOW DOWN

Item #	Device	Pc's	Power	Purchase	Erection
			kW	SEK	SEK
A 1301	PRESSTEAMED CHIP BIN	1	10		
A 1302	IMPREGNATOR	1	15		
A 1303	SCREW FEEDER	1	300		
A 1304	PRE HYDROLYSIS REACTOR	1	30		
A 1305	DEFIBRATOR	1	400		
A 1306	BLOW TANK 1	1		300,000	1,000
A 1307	BLOW TANK 2	1		300,000	1,000
A 1308	CONDENSER	1		100,000	1,000
A 1309	SO2 WATER TANK	1		50,000	500
A 1310	HEAT EXCHANGER	1		80,000	1,000
A 1311	RESIDUE/SUGAR PUMP	1	30	100,000	500
A 1312	RESIDUE/SUGAR PUMP	1	30	100,000	500
A 1313	GAS COMPRESSOR	1	10	300,000	3,000
A 1314	DOSING PUMP	1	5	80,000	3,000
A 1315	HEAT EXCHANGER	1		150,000	3,000
A 1316	HEAT EXCHANGER	1		150,000	3,000
A 1399	A 1301-A 1305 TOTAL	1		12,000,000	50,000

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #14 PRE-HYDROLYSIS WASH AND SEPARATION

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
A 1401	ROLLER PRESS	1	100	4,500,000	1,000
A 1402	ROLLER PRESS	1	100	4,500,000	1,000
A 1403	ROLLER PRESS	1	100	4,500,000	1,000
A 1404	SUGAR TANK	1		300,000	1,000
A 1405	RESIDUE TANK	1	15	400,000	1,000
A 1406	INTERMEDIATE SUGAR TANK	1		300,000	1,000
A 1407	RESIDUE TANK	1	15	400,000	1,000
A 1408	WEAK SUGAR TANK	1		300,000	1,000
A 1409	RESIDUE TANK	1	15	400,000	1,000
A 1410	WARM WATER TANK	1		300,000	1,000
A 1411	WARM WATER HEATER	1		100,000	500
A 1412	SUGAR PUMP	1	10	60,000	500
A 1413	SUGAR PUMP	1	10	60,000	500
A 1414	INTERMEDIATE SUGAR PUMP	1	10	60,000	500
A 1415	WEAK SUGAR PUMP	1	10	60,000	500
A 1416	WARM WATER PUMP	1	10	60,000	500
A 1417	RESIDUE PUMP	1	30	100,000	500
A 1418	RESIDUE PUMP	1	30	100,000	500
A 1419	RESIDUE PUMP	1	50	120,000	500

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #15 HYDROLYSIS REACTOR AND BLOW DOWN

Item #	Device	Pc's	Power	Purchase	Erection
			kW	SEK	SEK
A 1501	REACTOR HEAT EXCHANGER	1			
A 1502	REACTOR HEAT EXCHANGER	1			
A 1503	REACTOR HEAT EXCHANGER	1			
A 1504	2 ND STAGE REACTOR	1			
A 1505	ACID INJECTOR	1			
A 1506	BLOW TANK 1	1	20	500,000	2,000
A 1507	BLOW TANK 2	1	20	500,000	2,000
A 1508	BLOW TANK 3/FEED TANK	1	20	500,000	2,000
A 1509	CONDENSER	1		100,000	1,000
A 1513	ACID FEED TANK	1		120,000	1,000
A 1515	RESIDUE PUMP	1	50	120,000	500
A 1516	RESIDUE PUMP	1	50	120,000	500
A 1517	RESIDUE PUMP	1	50	120,000	500
A 1599	A 1501-A 1505 TOTAL	1		10,000,000	5,000

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

PROCESS AREA #16 HYDROLYSIS WASH AND SEPARATION

Item #	Device	Pc's	Power	Purchase	Erection
			kW	SEK	SEK
A 1601	DECANTER CENTRIFUGE 1	1	132	3,300,000	1,000
A 1602	DECANTER CENTRIFUGE 2	1	132	3,300,000	1,000
A 1603	DECANTER CENTRIFUGE 3	1	132	3,300,000	1,000
A 1604	FEED SCREW	1	20	50,000	500
A 1605	FEED SCREW	1	20	50,000	500
A 1606	FEDD SCREW	1	20	50,000	500
A 1607	SUGAR TANK	1		300,000	1,000
A 1608	RESIDUE TANK	1	20	400,000	1,000
A 1609	INTERMEDIATE SUGAR TANK	1	20	300,000	1,000
A 1610	RESIDUE TANK	1	20	400,000	1,000
A 1611	WEAK SUGAR TANK	1		300,000	1,000
A 1612	MGO HOPPER	1	10	50,000	500
A 1613	MGO SLAKING TANK 1	1	15	30,000	1,000
A 1614	MGO SLAKING TANK 2	1	15	50,000	1,000
A 1615	MGO SLAKING TANK 3	1	15	50,000	1,000
A 1616	SUGAR PUMP	1	15	60,000	1,000
A 1617	RESIDUE PUMP	1	30	100,000	1,000
A 1618	INTERMEDIATE SUGAR PUMP	1	15	60,000	500
A 1619	RESIDUE PUMP	1	30	100,000	1,000
A 1620	WEAK SUGAR PUMP	1	15	60,000	1,000
A 1621	MGO SLURRY PUMP	1	15	60,000	500

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #17 FERMENTATION

Item #	Device	Pc's	Power	Purchase	Erection
			kW	SEK	SEK
A 1701	SUGAR COLLECTING TANK	1	15	200,000	2,000
A 1702	PRE-FERMENTER TANK	1	30	500,000	300,000
A 1703	FERMENTER TANK	1	40	1,000,000	600,000
A 1704	FERMENTER TANK	1	40	1,000,000	600,000
A 1705	FERMENTER TANK	1	40	1,000,000	600,000
A 1706	COLLECTING TANK	1	10	60,000	5,000
A 1707	SCREEN	1	5	60,000	1,000
A 1708	SEPARATOR	1	50	600,000	10,000
A 1709	SEPARATOR	1	50	600,000	10,000
A 1710	SEPARATOR	1	50	600,000	10,000
A 1712	HEAT EXCHANGER	1		120,000	1,000
A 1713	SUGAR CIRCULATING PUMP	1	20	60,000	500
A 1714	PRE-FERMENTER PUMP	1	20	60,000	1,000
A 1715	PUMP	1	30	60,000	1,000

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

PROCESS AREA #18 ETHANOL DESTILLATION

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
A 1801	ETOH TANK	1	40	2,500,000	800,000
A 1802	HEAT EXCHANGER	1		200,000	2,000
A 1803	DESTILLATION COLUMN 1	1		2,000,000	200,000
A 1804	DESTILLATION COLUMN 2	1		3,000,000	250,000
A 1805	REBOILER	1		300,000	5,000
A 1806	ETHANOL COLLECTING TANK	1		80,000	1,000
A 1807	CONDENSER	1		300,000	10,000
A 1808	FEED PUMP	1	40	60,000	1,000
A 1809	ETHANOL PUMP	1	30	60,000	1,000

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #19 LIGNIN DRYER

Item #	Device	Pc's	Power	Purchase	Erection
			kW	SEK	SEK
A 1901	LIGNIN DRYER	1			
A 1902	CYCLON SEPARATOR	1	10		
A 1903	CONVEYER	1	5		
A 1904	CONVEYER	1	5		
A 1905	FEED SCREW	1	50		
A 1906	STEAM TURBINE	1			
A 1907	CIRCULATING FAN	1			
A 1908	SUPERHEATER	1			
A 1909	CIRCULATING FAN	1	250		
A 1999	LIGNIN DRYER TOTAL	1		30,000,000	2,000,000

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #20 BRIQUETTING

Item #	Device	Pc's	Power	Purchase	Erection
			kW	SEK	SEK
A 2099	BRIQUETTING TOTAL	1	100	4,000,000	200,000

SEDF / 91-07-26 **WOODHYDROLYSIS DEVICE LIST**

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #21 STEAM BOILER PLANT HIGH PRESSURE

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
A 2101	STEAM BOILER	1			
A 2102	CONDENSATE TANK	1			
A 2103	FEED WATER TANK	1			
A 2104	CAUSTIC TANK	1			
A 2105	SULPHURIC ACID TANK	1			
A 2106	DEMINERALISATION TANK	1			
A 2107	DEMINERALISATION TANK	1			
A 2108	CONDENSATE FLASH TANK	1			
A 2109	STEAM EJECTOR	1			
A 2110	LP GASIFIER	1			
A 2111	FORCED DRAFT FAN	1	70		
A 2112	INDUCED DRAFT FAN	1	70		
A 2113	FEED WATER PUMP	1	20		
A 2114	CONDENSATE PUMP	1	20		
A 2115	CONDENSATE PUMP	1	20		
A 2116	BOILER FEED WATER PUMP	1	50		
A 2117	STACK	1			
A 2199	BOILER PLANT TOTAL	1		19,000,000	2,000,000

SEDF / 91-07-26 WOODHYDROLYSIS DEVICE LIST

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

PROCESS AREA #22 WASTE WATER TREATMENT PLANT

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
A 2201	MIXING TANK	1	30		
A 2202	ANAEROB TANK	1	40		
A 2203	SLUDGE SEPARATOR	1	5		
A 2204	AEROB TANK	1			
A 2205	SLUDGE PRECIPITATOR	1	30		
A 2206	SLUDGE THICKENER	1	30		
A 2207	METHANE GAS FAN	1	30		
A 2208	FLARE	1			
A 2209	WASTE WATER PUMP	1	30		
A 2210	SLUDGE PUMP	1	20		
A 2211	SLUDGE PUMP	1	20		
A 2212	SLUDGE PUMP	1	20		
A 2213	DECANTER	1	50		
A 2214	AERATOR COMPRESSOR	1	50		
A 2299	A 2201-A 2214 TOTAL	1		20,000,000	5,000,000

SEDF / 91-07-26 WOODHYDROLYSIS DEVICE LIST

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #23 PLANT- AND INSTRUMENT AIR SUPPLY

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
A 2301	AIR COMPRESSOR	1	80	1,200,000	5,000
A 2302	AIR COMPRESSOR	1	80	1,200,000	5,000
A 2303	AIR DRYER	1	100	400,000	10,000
A 2304	AIR FILTER	1		50,000	
A 2305	AIR ACCUMULATOR	1		150,000	5,000

SEDF / 91-07-26 WOODHYDROLYSIS DEVICE LIST

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas. i.e., "stand-alone" facility

PROCESS AREA #24 STEAM BOILER PLANT LOW PRESSURE

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
A 2499	STEAM BOILER PLANT TOTAL	1	200	10,000,000	2,000,000

SEDF / 91-07-26 WOODHYDROLYSIS DEVICE LIST

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm, etc. (BASECASE)
Raw Material : Pine Saw Dust

Comments : Complete plant including all process areas.
i.e., "stand-alone" facility

PROCESS AREA #99 ELECTRICAL AND INSTRUMENT CENTRE

Item #	Device	Pc's	Power kW	Purchase SEK	Erection SEK
X 9999	Transformer 2 MVA	2		300,000	
Y 9999	Instrument system	1		1,000,000	

E.2 "Coupled" CASH Facility

- Wood Hydrolysis Cost Summary

SEDF / 91-07-29 **WOODHYDROLYSIS COST SUMMARY** 1/3

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.
Process type : 2 stage hydrolysis, ferm'n, distill, etc.
Raw Material : Pine Saw dust

Comments : Coupled Plant: i.e., no boilers, wastewater treat, air, briquetting, or chip preparation required

		SEK kKR
Production costs	: See page 3	44,593
Production credits	: See page 3	-30,650
Production overhead	: See page 3	14,750
ANNUAL PRODUCTION COST		28,693
ANNUAL CAPITAL COSTS	: See page 2	51,463
TOTAL ANNUAL COST		80,156

ANNUAL COST **3.59 SEK/l Ethanol**

SEDF / 91-07-29 **WOODHYDROLYSIS CAPITAL COSTS** 2/3

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.

CAPITAL COSTS : @ 100,000 ton/year DWS in feedstock			SEK kKR
ELECTRICAL AND INSTRUMENT CENTRE	Purchase		1,435
	Erection +Eng		4,965
FEED STORAGE	Purchase		10,275
	Erection +Eng		6,340
PRE-HYDROLYSIS REACTOR AND BLOW DOWN	Purchase		14,734
	Erection +Eng		14,723
PRE-HYDROLYSIS WASH AND SEPARATION	Purchase		17,700
	Erection +Eng		12,472
HYDROLYSIS REACTOR AND BLOW DOWN	Purchase		12,874
	Erection +Eng		16,960
HYDROLYSIS WASH AND SEPARATION	Purchase		13,594
	Erection +Eng		18,651
FERMENTATION	Purchase		7,079
	Erection +Eng		16,268
ETHANOL DESTILLATION	Purchase		10,068
	Erection +Eng		11,117
LIGNIN DRYER	Purchase		31,859
	Erection +Eng		11,639
BRIQUETTING	Purchase		4,419
	Erection +Eng		5,971
			243,141
Ratio feedstock 1.00 Raised to the power of 0.70			
SUBTOTAL			243,141
Contingency		15 %	36,471
Interest / construction		10 %	24,314
TOTAL			303,926
Capital cost/year	10 % interest and 10 year write off		49,463
Working capital	10 % of 20,000		2,000
GRAND TOTAL			51,463

ANNUAL CAPITAL COST **2.30 SEK/l Ethanol**

SEDF / 91-07-29 **WOODHYDROLYSIS PRODUCTION COSTS** 3/3

Location : Northern Ontario, Canada
Production : 22,335 m3/year Ethanol 95% conc.

PRODUCTION COSTS :						SEK kKR
Pine Saw dust	100,000	ton/year	a'	220	SEK/ton	22,000
Energy steam	640,780	GJ/year	a'	21	SEK/GJ	13,456
Power 60% of	28,409	MWh/year	a'	275	SEK/MWh	4,687
SO2	445	ton/year	a'	1,430	SEK/ton	637
HCl	523	ton/year	a'	1,320	SEK/ton	690
MgO	552	ton/year	a'	1,700	SEK/ton	939
CaO	959	ton/year	a'	1,080	SEK/ton	1,035
Nutrients Ferm	416	ton/year	a'	1,500	SEK/ton	624
Nutrients Waste	349	ton/year	a'	1,500	SEK/ton	524
Water	1,810,932	ton/year	a'	0.00	SEK/ton	
SUM						44,593

PRODUCTION CREDITS :						
Condensate	188,940	GJ/year	a'	21	SEK/GJ	-3,968
Lignin DWS	32,914	ton/year	a'	506	SEK/ton	-16,655
CO2	14,546	ton/year	a'	12	SEK/ton	-175
Methan	469,184	GJ/year	a'	21	SEK/GJ	-9,853
SUM						-30,650

Labour, Management, Repair, Maintenance and Insurance 14,750

GRAND TOTAL 28,693

ANNUAL PRODUCTION COST **1.28 SEK/l Ethanol**

E.3 Sensitivity Data for "Coupled" Facility

Appendix E.3

SENSITIVITY ANALYSIS

Ethanol Plant Coupled to Existing Pulp Mill

Effect of Feedstock Cost

Table E.1

base case: feedstock = $40/tonne or 220 SEK/tonne (dry basis)
Annual Capital Cost = $0.418/L (2.30 SEK/L)

Feedstock Cost ($/tonne)	Annual Production Cost of Ethanol (SEK/L)	Annual Production Cost of Ethanol ($/L)	Total Annual Cost ($/L)
-60	-1.18	-0.215	0.203
-40	-0.68	-0.124	0.294
-20	-0.19	-0.035	0.383
0	0.30	0.055	0.473
10	0.55	0.100	0.518
20	0.79	0.144	0.562
30	1.04	0.189	0.607
40	1.28	0.233	0.651
50	1.53	0.278	0.696
60	1.78	0.324	0.742
80	2.27	0.413	0.831
100	2.76	0.502	0.920

Effect of Lignin Credit

Table E.2

base case: lignin/cellulose fuel = $92/tonne or 506 SEK/tonne (dry)
Annual Capital Cost = $0.418/L (2.30 SEK/L)

Lignin Credit ($/tonne)	Annual Production Cost of Ethanol (SEK/L)	Annual Production Cost of Ethanol ($/L)	Total Annual Cost ($/L)
0	2.03	0.369	0.787
40	1.71	0.311	0.729
60	1.54	0.280	0.698
92	1.28	0.233	0.651
100	1.22	0.222	0.640
120	1.06	0.193	0.611
160	0.73	0.133	0.551
200	0.41	0.075	0.493

Effect of Price of Energy (i.e., steam etc., as based on oil price)

base case: steam energy = $3.8/GJ or 21 SEK/GJ (applies to steam, methane and condensate in result table)
Annual Capital Cost = $0.418/L (2.30 SEK/L)

Table E.3

CASE-A Feedstock cost and lignin price remain constant, independent of energy price (i.e., feed = $40/tonne, lignin = $80/tonne)

Energy Price ($/GJ)	Annual Production Cost of Ethanol (SEK/L)	Annual Production Cost of Ethanol ($/L)	Total Annual Cost ($/L)
2.5	1.29	0.235	0.653
3.1	1.29	0.235	0.653
3.8	1.28	0.233	0.651
4.5	1.28	0.233	0.651
5.0	1.28	0.233	0.651
6.0	1.28	0.233	0.651
8.0	1.27	0.231	0.649
9.1	1.26	0.229	0.647

Table E.4

CASE-B Feedstock cost remains constant, lignin price varies proprtionally to energy price

Energy Price ($/GJ)	Lignin Price ($/dry tonne)	Annual Production Cost of Ethanol (SEK/L)	Annual Production Cost of Ethanol ($/L)	Total Annual Cost ($/L)
2.5	60.5	1.55	0.282	0.700
3.1	75.1	1.42	0.258	0.676
3.8	92.0	1.28	0.233	0.651
4.5	109.0	1.14	0.207	0.625
5.0	121.0	1.04	0.189	0.607
6.0	145.0	0.84	0.153	0.571
8.0	193.7	0.44	0.080	0.498
9.1	220.0	0.22	0.040	0.458

Table E.5

CASE-C Both feedstock cost and lignin price vary proprtionally to energy price

Energy Price ($/GJ)	Feedstock Price ($/dry tonne)	Lignin Price ($/dry tonne)	Annual Production Cost of Ethanol (SEK/L)	Annual Production Cost of Ethanol ($/L)	Total Annual Cost ($/L)
2.5	26.3	60.5	1.21	0.220	0.638
3.1	32.6	75.1	1.25	0.227	0.645
3.8	40.0	92.0	1.28	0.233	0.651
4.5	47.4	109.0	1.32	0.240	0.658
5.0	52.6	121.0	1.36	0.247	0.665
6.0	63.2	145.0	1.41	0.256	0.674
8.0	84.2	193.7	1.53	0.278	0.696
9.1	95.7	220.0	1.60	0.291	0.709

Effect of Price of Electricity

Table E.6

base case: electricity = $50/MWh or 275 SEK/MWh
Annual Capital Cost = $0.418/L (2.30 SEK/L)

Elec. Price ($/MWh)	Annual Production Cost of Ethanol (SEK/L)	Annual Production Cost of Ethanol ($/L)	Total Annual Cost ($/L)
0	1.07	0.195	0.613
10	1.12	0.204	0.622
20	1.16	0.211	0.629
40	1.24	0.225	0.643
50	1.28	0.233	0.651
60	1.33	0.242	0.660
80	1.41	0.256	0.674
100	1.49	0.271	0.689

Effect of Hydrolysis Yield

Basecase: 50% glu/cell yield, 65% cellulose conversion

Table E.7

CASE-A Plant output maintained at approx. 22,400 m3/year by changing quantity of feed required

Glu/Cell Yield (%)	Cell. Conversion (%)	Feed Required (tonne/year)	EtOH Prod'n (m3/year)	EtOH Yield (L EtOH/tonne)	Annual Capital Cost (SEK/L)	Annual Prod'n Cost (SEK/L)	Annual Capital Cost ($/L)	Annual Prod'n Cost ($/L)	Total Annual Cost ($/L)
40	45	114500	22635	198	2.49	1.24	0.453	0.225	0.678
45	50	106500	22579	212	2.38	1.25	0.433	0.227	0.660
50	65	100000	22601	226	2.28	1.27	0.415	0.231	0.645
55	75	93700	22487	240	2.19	1.28	0.398	0.233	0.631
60	80	88400	22454	254	2.11	1.28	0.384	0.233	0.616
65	85	83600	22375	268	2.04	1.29	0.371	0.235	0.605

Table E.8

CASE-B Feed maintained at 100,000 tonne/year, plant output changes according to hydrolysis yield

Glu/Cell Yield (%)	Cell. Conversion (%)	EtOH Prod'n (m3/year)	EtOH Yield (L EtOH/tonne)	Annual Capital Cost (SEK/L)	Annual Prod'n Cost (SEK/L)	Annual Capital Cost ($/L)	Annual Prod'n Cost ($/L)	Total Annual Cost ($/L)
40	45	19894	199	2.59	1.35	0.471	0.245	0.716
45	50	21191	212	2.43	1.3	0.442	0.236	0.678
50	65	22601	226	2.28	1.27	0.415	0.231	0.645
55	75	24218	242	2.13	1.21	0.387	0.220	0.607
60	80	25655	257	2.01	1.17	0.365	0.213	0.578
65	85	26981	270	1.91	1.14	0.347	0.207	0.555

Effect of Fermentation Yield

Basecase: Fermentation Yield = 90% of theoretical

Table E.9

CASE-A Plant output maintained at approx. 22,400 m3/year by changing quantity of feed required

Ferm'n Yield (%)	Feed Required (tonne/year)	EtOH Prod'n (m3/year)	EtOH Yield (L EtOH/tonne)	Annual Capital Cost (SEK/L)	Annual Prod'n Cost (SEK/L)	Annual Capital Cost ($/L)	Annual Prod'n Cost ($/L)	Total Annual Cost ($/L)
60	149500	22236	149	3.04	1.32	0.553	0.240	0.793
70	128100	22461	175	2.71	1.29	0.493	0.235	0.727
80	112100	22412	200	2.48	1.28	0.451	0.233	0.684
90	100000	22477	225	2.29	1.27	0.416	0.231	0.647
95	94450	22411	237	2.21	1.27	0.402	0.231	0.633
100	89700	22433	250	2.13	1.25	0.387	0.227	0.615

Table E.10

CASE-B Feed maintained at 100,000 tonne/year, plant output changes according to fermentation yield

Ferm'n Yield (%)	EtOH Prod'n (m3/year)	EtOH Yield (L EtOH/tonne)	Annual Capital Cost (SEK/L)	Annual Prod'n Cost (SEK/L)	Annual Capital Cost ($/L)	Annual Prod'n Cost ($/L)	Total Annual Cost ($/L)
60	14983	150	3.43	1.72	0.624	0.313	0.936
70	17481	175	2.94	1.53	0.535	0.278	0.813
80	19979	200	2.58	1.39	0.469	0.253	0.722
90	22477	225	2.29	1.27	0.416	0.231	0.647
95	23726	237	2.17	1.23	0.395	0.224	0.618
100	24975	250	2.06	1.19	0.375	0.216	0.591